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Direktor: Prof.Dr.R.Hickel

Influence of various light curing regimes on the polymerization shrinkage and stress of dental restorative materials

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Anuradha Visvanathan
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Berichterstatter:	Prof. Dr. Karl-Heinz Kunzelmann
Mitberichterstatter:	Prof. Dr. Dr. h. c. Wolfgang Gernet Priv.Doz.Dr.Christof Holberg
Mitbetreuung durch den promovierten Mitarbeiter:	Dr. Nicoleta Ilie
Dekan:	Prof. Dr.med.D.Reinhardt
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Chapter 1
Definition of terms

Composites: Composites are physical mixtures of metals, ceramics, and / or polymers. The goal is to average the properties of the parts to obtain intermediate properties or take advantage of good properties of each part. The classic mixture for dental restorations involves ceramic particles mixed with a polymer matrix. This is commonly called *dental composite.*
Composites typically involve a dispersed phase of filler particles that are distributed within a continuous (matrix) phase.
A dental composite has traditionally indicated a mixture of silicate glass particle with an acrylic monomer that is polymerized during application. Development of modern dental composite restorative materials started in the late 1950s and the early 1960s, when Bowen began experiments to reinforce epoxy resins with filler particles. This work culminated in the development of the bis-GMA molecule.

Polymerization: It is a chemical reaction that transforms small molecules into large polymer chains (Anusavice, 1996). The polymerization of composite materials is never complete, that is a percentage of reactive groups do not participate in polymerization. The incomplete polymerization of a resin restorative material may predispose to material degradation. In addition, any surface layer exposed to air (oxygen) is incompletely polymerized. The same inhibition results in unreacted molecules that form the walls of pores within the bulk material. Degradation and wear of the

materials release components of the resin-based materials, which may cause reactions both locally and systematically.
Polymerization shrinkage: Monomer molecules are at intermolecular distances of 3 to 4 Angstrom units, but when they polymerize, the distance between the so formed polymer units is only 1.5 Angstrom units. This accounts for the shrinkage during the polymerization process (Peutzfeldt, 1997a)

Hardness: Hardness is the property that is used to predict the wear resistance of a material and its ability to abrade opposing dental structures. It is the "resistance to indentation". The indentation produced on the surface of a material from an applied force of a sharp point or an abrasive particle results from the interaction of properties like strength, proportional limit and ductility.

Elastic Modulus: The term elastic modulus describes the relative stiffness or rigidity of a material, which is measured by the slope of the elastic region of the stress-strain diagram.
If the tensile stress or compressive stress below a proportional limit is divided by its corresponding strain value, a constant of proportionality will be obtained that is known as the elastic modulus, modulus of elasticity or Young's modulus. Modulus of elasticity is given in units of force per unit area, typically giganewtons per square meter (GN/m^2), or gigapascals (GPa). There is a general consensus that filler contents should be maximised. The material's elastic modulus is of concern as well. Dental composites with high elastic modulus may no be able to accommodate to changes in tooth shape associated with flexural forces. This limitation could result in

debonding of the composite restoration from enamel or dentin. This situation is more critical for cervical restorations on facial surfaces where flexural stresses may produce large deformations. Flexible restorations (low elastic modulus) would be clinically more retentive because of improved accommodation to flexural forces. The opposite requirement would be true for large MOD restorations. Composites in those cases should be very rigid and thus minimize tooth flexure of the remaining cusps.

Gel point: It is the time at which the material gelates or reaches a semi-solid consistency. In this experiment, the time at which the force reaches 0.5 N is considered as an indirect measure of the gel point. This is the value obtained when the noise level from the machine is multiplied by a factor of ten.

Creep: Deformation with time in response to a constant stress is called creep (strain relaxation).

Chapter 2

Introduction

The days of amalgam are gone when the more aesthetic tooth like composite material is being used as a restorative material. When monomers are converted to polymers it will lead to shrinkage of the material causing residual contraction stress. Stress results in one or more of the following consequences namely micro leakage, secondary caries, marginal loss, adaptation loss, enamel micro cracks and post operative sensitivity.

Types of composites:

Composite can be classified based on the filler particle size as:

Macrofillers- 10 to 100 microns

Midifillers- 1 to 10 microns

Minifillers- 0.1 to 1 micron

Microfillers- 0.01 to 0.1 micron

Nanofillers- 0.0005 to 0.01 micron

Composites are grouped on the basis of

1. Range of average particle size,
2. Whether or not they are hybrid due particle size mixing
3. Whether the composite is a homogeneous mixture of filler and resin or a heterogeneous mixture including pre-cured composite.

Chemistry:

1. ***Resin matrix:***
    i. Bis-GMA , bisphenol a-glycidyl methacrylate
    ii. UEDMA, urethane dimethacrylate

iii. TEGDMA, tri-ethylene glycol dimethacrylate
iv. Photo initiator- camphoroquinone (wavelength-400 to 500 nm)
v. Inhibitor- butylated hydroxytoluene
vi. Optical modifiers- titanium dioxide and aluminium dioxide.

2. ***Filler Particle***: Incorporation of filler particles into the resin matrix significantly improves the properties of the matrix material if the filler particles are well bonded to the matrix. To enable bonding of filler particles to the matrix, a coupling agent is required. Fillers can be quartz or silica (colloidal or pyrogenic).

3. ***Coupling agent***: As mentioned above, it is important that the filler particles remain bonded to the resin matrix. This allows the more flexible polymer matrix to transfer stresses to the stiffer filler particles. The bond between the two phases of the composite is provided by the coupling agent. Organosilanes such as gamma- methyacryloxypropyltrimethoxy silane are more commonly used.

Photo initiators: Traditionally, adhesive and resin composite systems contained camphoroquinone (CQ), a visible-light-sensitive diketone photo initiator responsible for initiating free-radical polymerization. CQ absorbs energy in the visible-light region of 400 to 500 nanometers with a peak at 468 nanometers. Photons associated with this frequency range will be absorbed by the camphoroquinone, raising it from the ground state to an excited, but short-lived, activated triplet state. When an excited triplet bumps into an amine co-initiator, an aminoalkyl free radical forms, which is capable

of initiating polymerization. In a few products, new photo initiators have been introduced by manufacturers to reduce the intensity of the yellow color of the composite resin restorative material typically produced with the addition of camphoroquinone or to prevent the inactivation of the amine co-initiator by acidic monomers contained in some enamel and dentin adhesives. These new photo initiators absorb light energy in lower regions of the visible-light spectrum. Examples would be phenyl-propanedione (PPD) and Lucirin TPO.

Light curing units:

Light energy may be provided by four types of curing lights: Quartz-Tungsten-Halogen (QTH), Light-Emitting Diode (LED), Plasma-Arc (PAC) or Argon Laser. Composite can be chemically cured, dual cured or light cured. Light cured composites are more widely used in the clinical practice for restoring the teeth. As the composite material undergoes various developments, the methodology of curing also develops at a rapid pace. Previously, ultraviolet lamps were used for curing. These were replaced by the visible light curing lamps like halogen, light emitting diode, plasma lamps, lasers etc,. The different kinds of lamps have improved light intensity, wavelength, handling characteristics. It has been found that increasing the light intensity in order to decrease the time required for curing causes more contraction stresses. This is disadvantageous as this will endanger the bond strength. Therefore, lower intensity is preferred in terms of stress minimization. Lower intensity means low degree of conversion which is more likely to leave behind unreacted double bonds and unreacted monomers causing biocompatibility problems. When neither high intensity nor low intensity is preferred, an intermediate intensity will be able to suit

the requirements for a safe restoration. Such an intermediate power is been incorporated in most of the modern light curing unit, be it a halogen or a light emitting diode. This facility is called the soft-start. This can be full intensity of light with gap intervals of no light, or by starting under low power followed by high power. Many modifications are possible in the soft–start mode for experimental purposes.

The most common dental curing light in use today is the QTH. The relatively broad emission spectrum of QTH curing lights allows them to initiate the polymerization of all known composite resin materials available. The principle output from these lamps is infrared energy with the generation of high heat. Filters are used to reduce the heat energy to the oral structures and provide further restriction of visible light to the narrower spectrum of photo initiators. Finally, a silver-coated dichroic reflector passes infrared energy out the back and reflects and focuses the light forward to provide a focal area of energy at a defined distance. Ultimately, 99.5% of the original radiation is eliminated. Due to the high operating temperatures, the QTH bulbs have a limited lifetime. The reflector, bulb and filters can break down over time, reducing the curing effectiveness. At the same time that new photo initiators were being introduced in restorative materials, dental product manufacturers began developing new curing lights with light-emitting diodes (LEDs). LED curing lights use special semiconductors for the electroluminescence of light rather than the hot filament found in QTH lights. This provides a longer life span, consistent output and lower power consumption significant ultraviolet or infrared light is emitted thereby reducing lateral heat and minimizing the need for a noisy fan. Since the energy is clearly defined by the semiconductor, most of the light emitted is

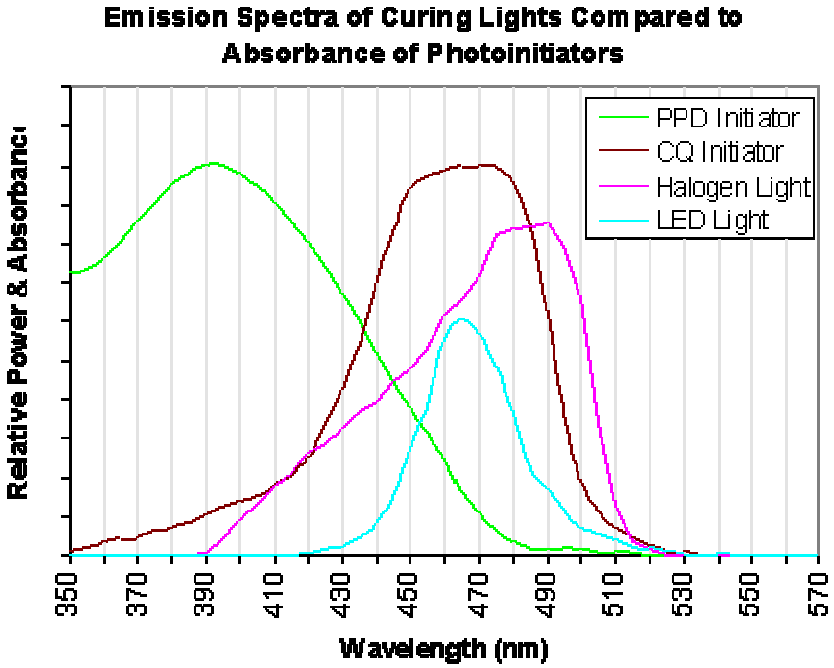
concentrated in a narrow band around 470 nanometers which is ideally suited for composite resins that use the photo initiator camphoroquinone. However, the emission spectrums from LED curing lights are so narrow; they may not be absorbed by the new photo initiators. The newest generation of LED lights have irradiance and degree-of-cure similar to the most popular QTH lights.

Plasma-arc (PAC) lights generate a high-voltage pulse that creates hot plasma between two electrodes in a xenon-filled bulb. The irradiance (up to 2400 mW/cm^2) is much higher than typical QTH or LED lights, but the PAC lights generate very high heat with an inefficient emission spectrum similar to QTH curing lights. Filters limit the emission spectrum to the blue spectrum. Most new plasma-arc lights have broad spectrums and should be absorbed by all photo initiators.

Light emitted from an argon laser is very different from that emitted from QTH or PAC lights. The photons produced are coherent and do not diverge, therefore they concentrate more photons of specific frequency into a tiny area. The emission spectrum is very narrow and compatibility problems with some photo initiators can be anticipated.

The following graphs compare the emission spectra of an LED light & a halogen light to the approximate absorption spectra of PPD & CQ photo initiators:

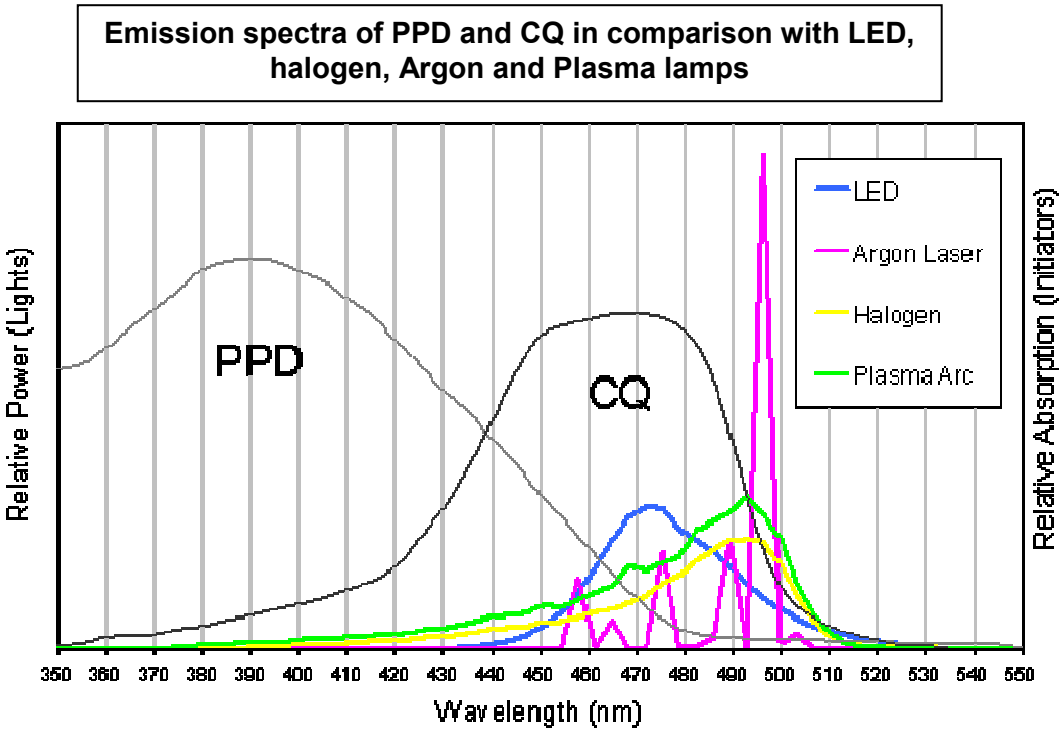
Graph 2.1: Emission spectra of curing lights and initiators



The emission peak of LED light coincides with the absorption peak of CQ, but does not overlap the sensitive wavelengths of PPD.

Halogen light has a broader output, overlapping sensitive wavelengths of both CQ & PPD.

Graph 2.2: Emission spectra of initiators and different types of light curing lamps.



Polymerisation shrinkage and stress:

Polymerisation shrinkage occurs when the dental composite is cured. 'Cure' is to change the properties of the resin by chemical reaction, for example, by condensation, polymerisation or addition. The reaction may be accompanied by the action of heat with or without pressure.

Resin systems shrink during polymerisation mainly because the monomer molecules are located at Van der Waals distances (4 Angstrom) from one another while the corresponding polymers are within a covalent bond

distance to each other. Thus in the polymer, atoms are closer to one another. Polymerisation shrinkage is mainly the result of rearrangement of the molecules into less space that was required for the liquid phase of the mobile monomer.

The direction of contraction depends on a number of factors. If contraction occurs at the same instant and is homogeneously distributed throughout the material one can expect a deformation that is free of stress, however if the contraction is hindered by cavity design or bonding to the cavity, little can be said about the internal movements of the material. Either the material will yield without stress to the cavity wall or it will be separated from the wall. On the other hand, the result may lie between two extremes and cause internal stresses, if the material possesses enough plasticity, these stresses will disappear due to flow (Davidson and De Gee, 1984).

The shrinkage creates tensile stresses as high as 130 kg/ cm2 at the interface between the resin and the tooth. Stress is the force with which a structure resists an external load placed on it. It is the internal reaction to an externally applied load and is equal in magnitude but opposite in direction to the external load. Although technically the internal force, this is difficult to measure and so the accepted way of measuring stress is to measure the external load applied to the cross sectional area, measured in force per area in units such as Kg/ cm^2, MPa, MN/m^2 or psi.

$$\sigma = F/A$$

where, σ is the stress, F is the force and A is the cross sectional area.

AIM OF THE STUDY:

As more and more dental composites with different properties and qualities enter the clinics, this study was aimed to experiment the polymerisation shrinkage stress and mechanical properties of the microhybrid and nanocomposites .The composites which are studied are Tetric Ceram, Tetric Evo Ceram, Filtek Supreme and Venus. A comparison of each of these composites among themselves and attaining an overall view of material properties is also aimed.

Chapter 3

An insight into polymerization shrinkage and stress

Methods to determine polymerisation shrinkage and stress:

There are two basic approaches to determine shrinkage of a material.

A. Volumetric dilatometry: Here, measurements of volumetric shrinkage are usually made indirectly in a dilatometer by determining the linear height changes in a column of fluid (mercury or water) connected to a reservoir surrounding the test substance.

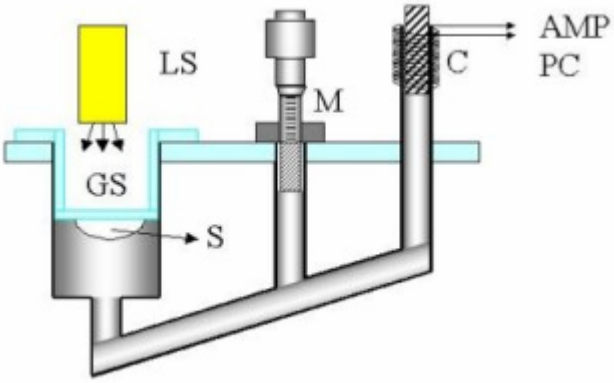
B. Non-volume dilatometry: These measurements are usually made of one-dimensional or possibly two-dimensional strain in the material, by means of a contacting or non-contacting transducer.

1.Mercury dilatometer (De Gee *et al,* 1981, Penn, 1986, Feilzer *et al,* 1988, Iga et al 1991). This is the first and foremost device to determine the polymerisation shrinkage of resins. It was in 1981 that A.J.de Gee et al deviced this equipment. Mercury dilatometer determines both the pre and post gel shrinkage. The equipment is less influenced by the flow ability of the resins. The difficulties encountered in using this device was that it provided less access to the light curing unit, critical temperature control was mandatory, effect of exotherm from the polymerisation reaction affected the temperature of the fluid used, more composite was needed for the experiment than that is required clinically for a restoration, total shrinkage was measured along with the storage modulus which can be misleading and there is a potential risk of mercury vapour. Dilatometry is laborious and

time-consuming and is also subject to data scattering when used for low viscosity resins.

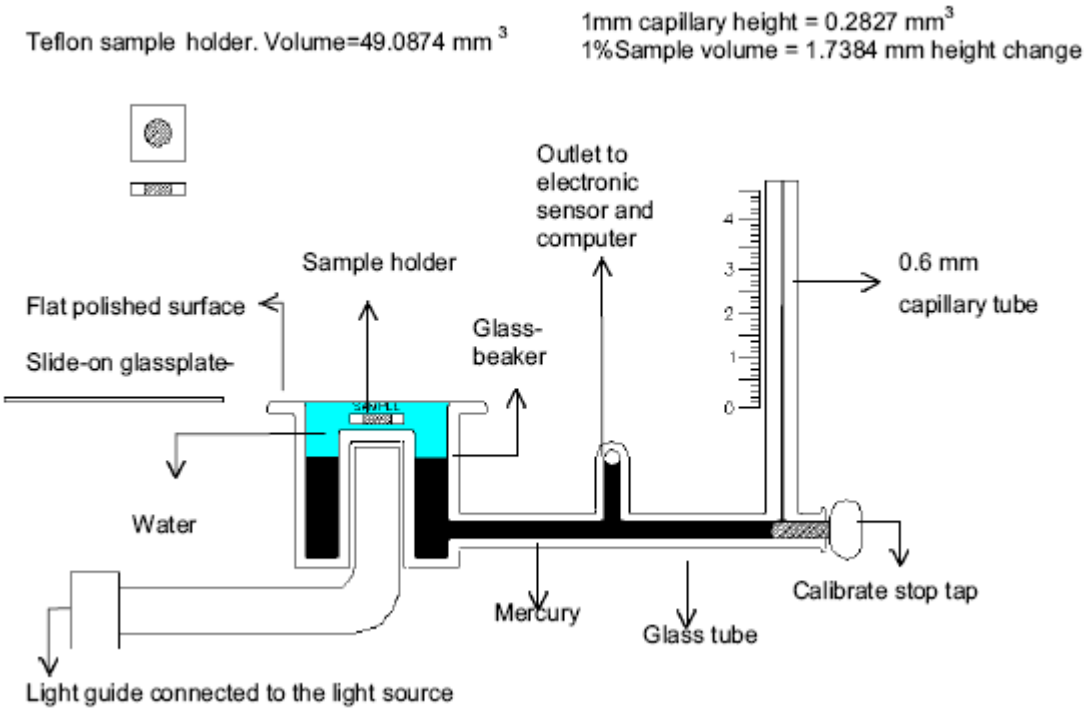
A modified mercury dilatometer is described where any change in the volume of the sample is registered every 0.5 s as a change of the mercury height in the capillary, which is measured electronically instead of by the naked eye. It consists of a glass stopper (GS), open at the top to allow access of the light guide of the light source. The sample (S) is positioned underneath the glass stopper. Micrometer screw (M) for calibration is used. There will be a coil (C) with core inside the glass tube, floating on the mercury, connected to an electronic device (AMP) and computer (PC).

Figure 3.1: Schematic representation of mercury dilatometer



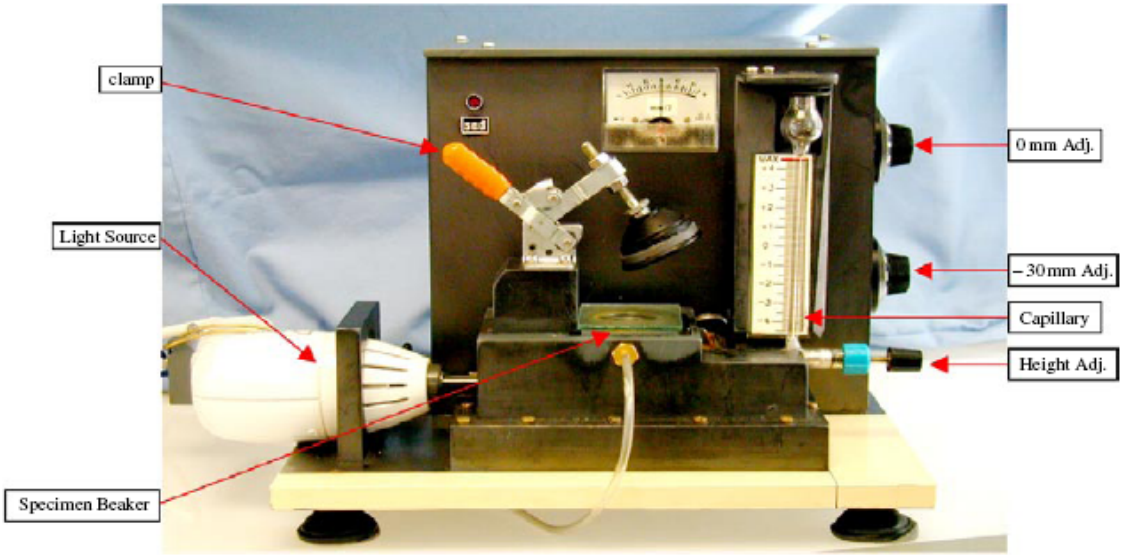
It was concluded that with this modified dilatometer reproducible measurements can be obtained, thus, the instrument is particularly suitable for the study of light-curing dental resins.(Oberholzer *et al,* 2002)

Figure 3.2



(Oberholzer *et al,* 2002)

Figure 3.3 : Modified mercury dilatometer



(Oberholzer *et al,* 2002)

2. Water dilatometer (Bandyopadhyay, 1982;Lai and Johnson, 1993;Rees and Jacobsen, 1989):Water dilatometers are similar to mercury dilatometer except that the fluid in the capillary is water and not mercury. Resin samples may be affected by the water and may not polymerise efficiently.

3. Deflecting disc method (Bausch *et al,* 1982;Watts and Cash, 1991): Shrinkage is measured indirectly by monitoring the deflection of a thin glass cover slip, held in contact with the surface of the composite specimen through surface energy and adhesion while supported along its outer radius by a brass ring. A LVDT transducer is used. This method measures dimensional change along a single axis and yields values comparable to the mercury dilatometer.

4. Modified bonded disc method/ Bonded disc method (Sakaguchi *et al,* 2004c): This method uses a load cell which measures the force necessary to restrict the shrinkage after curing. This measurement is useful in detecting the polymerisation stress.

5. Optical methods: A device by name Accuvol (Sakaguchi *et al,* 2004b) captures a digital video image of the external outline of a rotating specimen as it cures. Changes in the specimen volume are calculated from the area digitized by the camera.

6. Linometers (de Gee *et al,* 1993;Feilzer *et al,* 1989) determined linear contraction by means of a contact less displacement transducer. It measured the total shrinkage (pre shrinkage *plus* post gel shrinkage). The dilatometer records the volumetric change which proceeds freely in the mercury bath whereas the linometer records dimensional change in one direction in which

the free shrinking condition is achieved by separating the materials from the aluminium and glass surfaces with grease. The linometer unlike the dilatometer is insensitive to temperature fluctuations and therefore accurate temperature control is not necessary. This linometer can be assumed as a modification of the deflecting disk method. The device tracks the linear vertical motion of a free floating metallic target fixed to the surface of a composite specimen applied to a horizontal glass plate, as opposed to measuring the vertical deflection of a horizontal glass cover slip, as previously described in the deflecting disk method.

7. Strain gages: This device measures shrinkage only after the composite develops elastic properties (Sakaguchi *et al,* 1997).

8. Thermo mechanical analyser method (Sakaguchi *et al,* 2004a): A quartz dilatometry probe measures the displacement at surface of the composite material. Shrinkage values are obtained by dividing specimen displacement by its height.

9. Specific gravity measurements and Density change methods (Hay and Shortall, 1988;Puckett and Smith, 1992;Rueggeberg and Tamareselvy, 1995):Total amount of volumetric shrinkage (pre-and post-gel) were established.

10. Laser interferometric method (Fogleman *et al,* 2002): The laser interferometric method monitors the linear polymerization shrinkage in dental restoratives. The apparatus consists of a low power Helium-Neon laser, a home-built Michelson interferometer, amplified photodiode detectors, and a computer data acquisition system. The 'interferograms' are

converted into percent linear contraction a profile that reveals the relative kinetics of material shrinkage. Interferometry offers several advantages over conventional methods of measuring polymerization contraction. The advantages include the inherent sensitivity and accuracy offered by interferometric measurements; the instrument does not need to be calibrated since the wavelength of the laser light source provides an accurate length standard. Also, the ability to collect data at high acquisition rates allows for the real-time characterization of unusually fast photo polymerization reactions. The low cost and relative ease of use associated with the apparatus are also advantageous.

11.Laser beam scanning (Fano *et al,* 1998): A non-contact method used for measurement of linear dimensional variation.

12.Gas pycnometer: (Cook *et al,* 1999): A gas pycnometer was used to determine the volumes of specimens prior to and after photo polymerization and from which the total volumetric shrinkage could be determined. {The percentage of shrinkage (P) was calculated by P = 100 (SVi – SVf) / SVi where the suffixes *i* and *f* indicate the measurements before and after polymerization, respectively. SVi is initial specific volume, given by SVi =volumei/massi, and SVf is final specific volume, given by SVf= volumef/massf given by SVf= volumef/massf} This method is appropriate for shrinkage measurements where only the total amount shrinkage is required and in particular for the measurement of shrinkage of photo cured materials which are sensitive to water absorption.
The equipment accomplishes the measurement of skeletal volumes by observing the reduction of gas capacity in the sample chamber caused by the presence of the sample. This instrument does not have active temperature

control of the measurement chamber, but employs a large thermal mass to enable passive regulation of the temperature in the measuring chamber and the expansion chamber to less than ±0.01°C. Thus, the temperature is considered constant while the measurements are done. Helium is an inert gas and it can penetrate in the surfaces pores of the material whereas mercury and water cannot.

13. Hounsfield and ACTAIntense Tensilometers (Dauvillier *et al,* 2000): Hounsfield and ACTAIntense are both an automated servo-controlled universal testing machine, the former is a commercial device and the latter a device build for experimentation at ACTA (Netherlands). They are useful for measuring static and dynamic experiments but are less useful in determining the axial shrinkage strain. The universal testing machine is capable to measure the shrinkage load development of the setting composite in a longitudinal direction.

14. Stress-Strain analysers (Chen *et al,* 2001a): Stress is being measured in a Stress Strain Analyser using the basic principle of universal testing machine.

15. Photo elastic analysis: (Ernst *et al,* 2004a; Kinomoto and Torii, 1998): This method uses polarised microscopy which determines the polymerisation stress.

Stress distributions can be studied by

1. Photo elastic modelling

2. Finite Element analysis.

Factors affecting or influencing polymerisation shrinkage and stress:

1. ***Material nature***: Composite consists of the matrix resin Bis GMA and its derivatives. Bis-GMA is a heavy molecular weight oligomer with high viscosity, so diluents like MMA, Bis DMA, UDMA and TEGDMA or EGDMA are added but they potentially cause polymerization shrinkage. To decrease the effects of the diluents, fillers are added thereby reducing the percentage of volume of the resin matrix. Filler load, filler volume, filler size and filler weight are critical. The lowest maximum polymerization contraction force is for the chemical cured composite and the hybrid composite recorded the highest contraction force. Those of the microfills were intermediate (Bouschlicher *et al,* 1997b).

2. ***Resin Chemistry***: Composites can be cured by

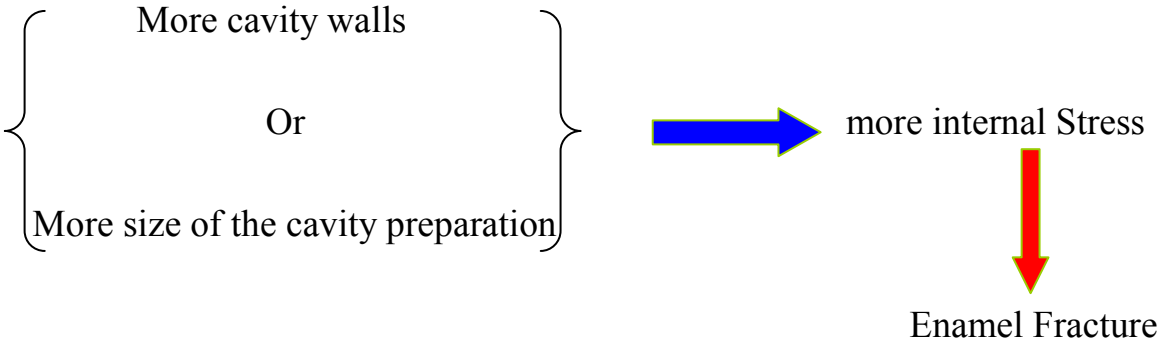
i. Free radical polymerization

ii. Cationic polymerization-(oxiranes and siloranes)

There is possibility to decrease the polymerization shrinkage due to expandable monomers.

3. ***Configuration factor & geometry*** (Feilzer *et al,* 1987b)

SHRINKAGE → STRESS ON THE CAVITY WALLS



Due to enamel fracture, white lines appear on the restoration upon polishing as the debris accumulates in the open cracks.

The magnitude of polymerization contraction stress will be configuration dependent. Configuration factor or C-factor is the ratio of bonded surfaces to the unbonded surfaces (Feilzer *et al,* 1987c). Maximum forces are inversely related to the C-factor (Bouschlicher *et al,* 1997a). Conversely, a study conducted by Kunzelmann et al shows that shrinkage forces are dependent on distance rather on the configuration (Kunzelmann and Hickel, 1990).

4. ***Modulus of elasticity***: High modulus of elasticity is one of the several factors which lead to high contraction stresses (Unterbrink and Liebenberg, 1999).

5. ***Degree of conversion of monomer***: Degree of conversion denotes the number of monomer units that are joined together in a polymer. It is the final C=C conversion. It can be detected by FTIR (Fourier Transform Infrared

Spectroscopy), Raman spectroscopy or HPIC (High Performance Liquid chromatography).

6. ***Rate of polymerization***: It is preferred to slow down the rate of polymerization and thereby prolong the time until the gel point. It has been observed that the longer the pre-gel point, the lesser is the stress in the post gel phase (Versluis *et al,* 1998).

7. ***Light-mode, source, intensity, duration, distance & direction:***

In the field of dental composites different light curing units (LCU) such as the conventional and the high intensity (quartz tungsten) halogen lamps, both producing white light, light emitting diodes, producing blue light, the plasma lamps and the lasers are used (Althoff and Hartung, 2000;Dunn and Bush, 2002;Peutzfeldt *et al,* 2000). All of them are undergoing a constant evolution.

The performance of light curing devices and the degree of polymerization in relation to light intensity, irradiation time, the size, distance and orientation of the tip of the source, shade, layer thickness and composition of the material have been evaluated by various researchers (Bennett and Watts, 2004;Harrington and Wilson, 1993;Lindberg *et al,* 2004;McCabe and Carrick, 1989).

According to Althoff and Hartung (Althoff and Hartung, 2000) the efficiency of the light curing units depends on the total energy concept. This concept explains that for efficient polymerization of composites, both intensity and photo-initiation time are important. When adequate curing with short curing time is desired, a higher intensity is required. A higher intensity also means higher polymerization shrinkage stress at the tooth-restoration

interface and micro leakages. (Dennison *et al,* 2000; Feilzer *et al,* 1995a; Lösche1999; Stritikus and Owens, 2000; Unterbrink and Muessner, 1995b). Optimal setting of an average-sized composite restoration requires a certain quantity of light energy. The amount of energy depends on the characteristics of the light source used and the time of irradiation. Swift conversion with high-energy lamps is proportionally accompanied by rapid hardening and could negatively affect the marginal integrity of the adhesive restoration. (Davidson and De Gee, 2000).It is at this stage that the concepts of soft start polymerization or ramp polymerization gained importance. In the soft start method the composite is cured at a lower intensity initially, followed by high intensity. This in turn, increases the time until gelation (gel point) and thereby gives more time for the material to flow and hence compensates the initial polymerization shrinkage stress, resulting in a better bond (Feilzer *et al,* 1990).

The study conducted by (Lim *et al,* 2002) suggested that a slow curing reaction results in a prolonged period before gelation and slow development of material stiffness. A two step polymerization reduces the polymerization shrinkage strain by prolonging the gel-phase of a resin composite during its early polymerization process and it has statistically significant difference in lowering polymerization shrinkage stress in comparison with standard methods (Ernst *et al,* 2000c; Ernst *et al,* 2003).

It has been reported that a low initial polymerization rate improves the quality of marginal adaptation (Rahiotis *et al,* 2004). It has been found that the initial cure of the soft start polymerization has no influence on the micro hardness, but can increase the flexural modulus and flexural strength and yield better marginal integrity (Mehl *et al,* 1997) and that although the high-intensity curing provided rapid curing, a two-step curing provided better

marginal integrity (Burgess *et al,* 1999). In one of the studies by Koran et al. (Koran and Kurschner, 1998) it was inferred that the ramp curing affected neither the shrinkage nor the mechanical property such as hardness of the composites when the total irradiation dose is comparable to a fast cure or continuous cure protocol so that an adequate degree of conversion is achieved. They also concluded that above a total irradiation dose of 17,000mWs/cm², the surface hardness values remain constant and will be increased no further. Studies exist, demonstrating the positive influence of the soft-start polymerization approach (Ernst *et al,* 2000b;Ernst *et al,* 2000a;Ernst *et al,* 2003;Feilzer *et al,* 1995b), while some newer studies deny this effect (Hofmann *et al,* 2003;Sahafi *et al,* 2001). The positive aspect of soft–start was not accepted by some authors because it is considered that the bonding agents are more important rather than the soft-start procedure itself. From these references, it is apparent that soft start curing has been widely explored for improving the marginal integrity of the composites which in turn is influenced by the polymerization shrinkage stress.

Yet another important factor in the material properties of composites is the degree of hardness. The hardness at the top surface is higher compared to the bottom. This is because of the fact that the polymerization depth is directly related to the thickness of the composite and is influenced by the light intensity (Sobrinho *et al,* 2000) and the exposure time (Baharav *et al,* 1988). The intensity of light determines the degree of hardness after the polymerization especially at the surface of the composite which is farther from light source at a clinically relevant thickness of 2 mm. A low intensity of the light source would result in a less hardened material (Pires *et al,* 1993).

8. ***Temperature***: In a study conducted by (Bausch *et al,* 1981) it was showed that higher temperature will improve the mechanical properties of the composite and actually suggests heating of the composite before restoration. Heating improved the cross-linking of the polymer structure.

9. ***Porosity***: Void in composites not only decreases the polymerization shrinkage but also the strength and hardness which is not desirable (Feilzer *et al,* 1993).

10***. Flow properties*** (Feilzer *et al,* 1990): When the resin composite is capable of flow during the initial stages of polymerization reaction, the polymerization shrinkage is less as compared to a rigid non-flowable. However, the flowables contain low amounts of filler and more of the resin, which leads to high polymerization shrinkage. However, he contraction stress is lower for the low filled material. Thus although the low filled material has a larger volumetric shrinkage, it can develop a lower contraction stress. The origin of this effect can be found in the E modulus. E-modulus of the high filled material reaches a considerable value in an early stage of the reaction itself (Aarnts *et al*, 1999)

11. ***Techniques***: Poskus *et al,* 2004 showed that incremental technique is preferable to bulk method as far as mechanical properties such as hardness are concerned.

12***. Bonding agents:*** Bonded restorations are prone to more accumulation of stress than unbonded restorations. Bonding restricts the degree of flow.

13***. Water sorption:*** Composites containing zinc and barium glasses have shown to be more susceptible to aqueous attack than those containing quartz.

Zirconia silicate fillers are also susceptible to aqueous attack. This may be compounded by the smaller filler surface area associated with the spherical shape of zirconia/silica fillers that may decrease bonding of fillers to the resin matrix. Volume percent of the filler content, the amount of residual monomer or matrix polymer also have effect on the water absorption.

The mechanism of hydrolytic degradation is enhanced if the filler particles have metallic ions in their composition. The explanation of this effect is that some ions in the filler particles, such as zinc and barium, are electropositive and tend to react with water. With the loss of these elements into water, the charge balance inside the silica network is changed and re-established with the penetration of hydrogen ions of the water in the spaces occupied by the zinc and barium. As a result of the increase of the concentration of hydroxyl ions, the siloxane (Si-O-Si) bonds of the silica network start to break, and there is formation of an autocatalytic cycle of surface degradation. This mechanism would explain the continuity of the superficial softening with aging time. It has been suggested that resistance to initial softening will improve the abrasion resistance of dental composite restorations.

Water is considered as a plasticizing agent. However storage of set composites in water for 24 h improves the surface hardness value (Ilie, 2004).

Strategies to reduce shrinkage:

a) Increased volume of filler.
b) Use of bulk fillers such as ceramic inserts to decrease the volume of the material that shrinks.

c) Stress relief-nonbonded nanofillers/DBA/HDPE.
d) Use of stereo isomeric alicyclic spirorthocarbonates which expand, cyclopolymerizable monomers and monomers with low volumetric shrinkage (Stansbury, 1990;Stansbury, 1992a;Stansbury, 1992b;Stansbury *et al,* 1995;Stansbury and Antonucci, 1992)
e) Silorane & oxirane technology: Oxiranes are cyclic-3 membered ethers. For oxiranes the polymerization is not inhibited by oxygen but by the presence of high humidity or basic materials such as Fe $(OH)_3$. They have an intrinsic 'soft-start' phenomenon. 1, 3-bis [(p-acryloxymethyl) phenethyl] tetramethyldisiloxane (BAPD) was a high molecular weight monomer with low viscosity which does not require diluents that can potentially increase the polymerization shrinkage. It has properties comparable to Bis GMA(Lai *et al,* 2004).
f) Ormocers with multifunctional urethane & thioether (meth) acrylate (Chen et al, 2001) & Ceromers: Ormocers are **Or**ganically **Mo**dified **Cer**amics. They contain a main chain made up of inorganic glass Si-O-Si and an organic side chain. On the other hand, Ceromers are **Ce**ramic **O**ptimized Poly**mers** which consist of an Organic 'C' main chain with an inorganic side chain and other multimetharylates (Wan *et al,* 2001).
g) Improved Photo-Initiators.
h) Stress absorbing liners.
i) Fluoride releasing monomers : These help in mitigating the negative effects of marginal gaps.(Peutzfeldt, 1997b).

j) Light curing unit with lower intensity: It has been proved that high intensity lamps have deleterious effect on the properties of the restoration(Unterbrink and Muessner, 1995a).

k) Incremental or bulk filling: Contradicting views are present as to whether composite should be bulk cured or incrementally cured. Incremental curing may not decrease the shrinkage stress as expected as it tends to deform the cavity walls during each increment and thereby decreases the actual amount of material needed for the restoration (Versluis *et al,* 1996).

Chapter 4

Materials and Methods

The polymerization shrinkage force of the dental composites are measured in a Stress–Strain-Analyzer (SSA T80, Engineering Consultancy, Peter Dullin, Jr, Munich, Germany).The test set up has been explained previously in the work of (Chen *et al,* 2001).

The basic working parts of SSA consists of a

1. ***Piezo-actuator*** (Model: P-246.50, Physik Instrumente PI GmbH and Co. Waldbronn, Germany): Actuators are devices that produces motion (displacement). It is a device that controls the movement of mechanical action of a machine indirectly rather than directly or by hand. Piezoelectric materials are those which change their dimensions when a voltage is applied and produce a charge when pressure is applied. In this experiment a Piezo-translator was being used which produces linear motion.

2. ***Load-sensor****-2000N* (Model: 8438, Burster Präzisionsmeßtechnik, Gernsbach, Germany)

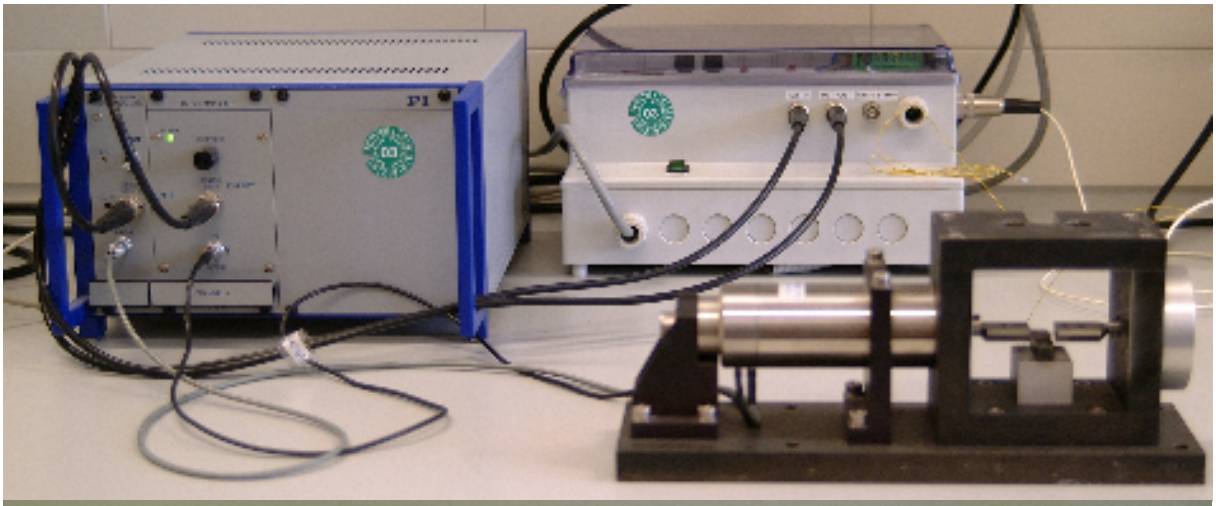
3. ***Photo sensor or photodiode***: A sensor which helps to start the data recording exactly when photo-initiation occurs. Between the load sensor and the piezo actuator is a stage on to which the photo-diode is mounted.

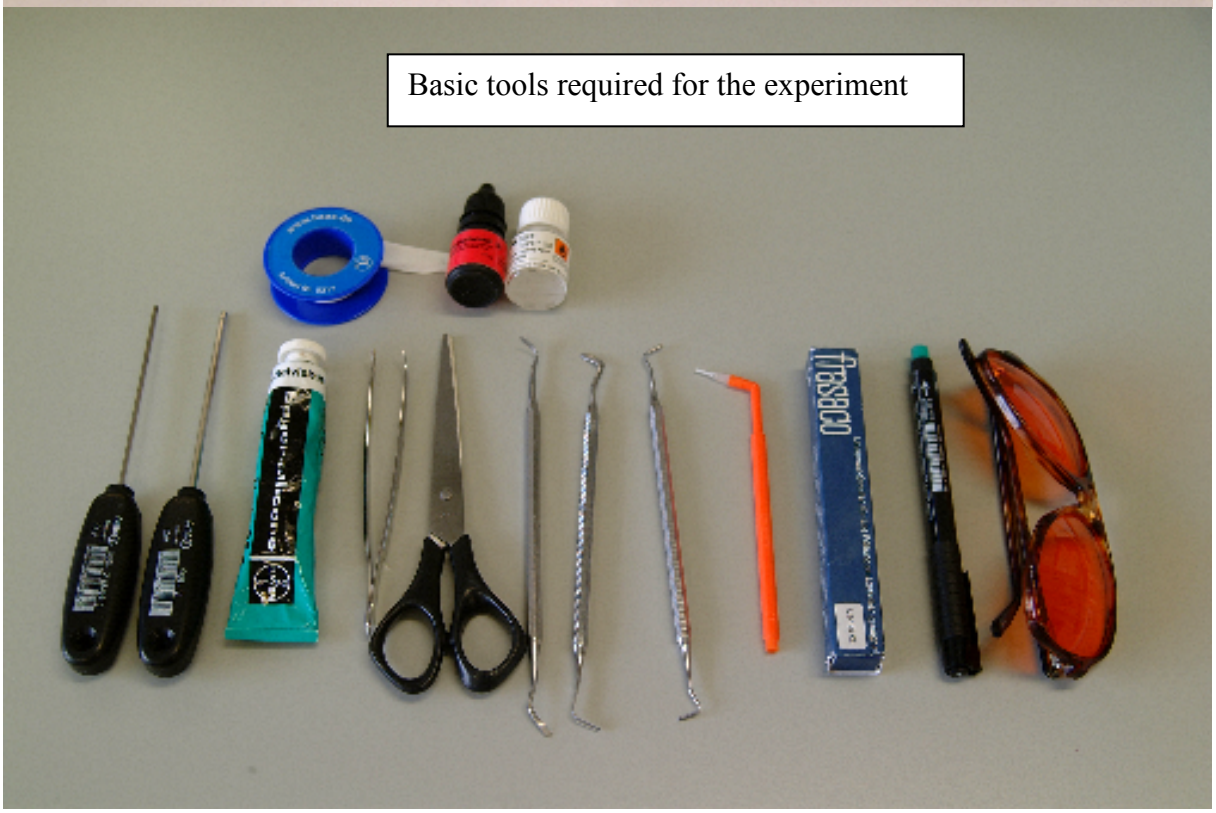
4. ***Piezo control unit***: This consists of the position sensor.

5. ***Signal conditioner***: This is an amplifier following the sensor which prepares the signal for succeeding amplifiers, transmitters, etc. It may also supply power for the sensor.

6. ***Data Acquisition Card***: Data acquisition is the sampling of the real world to generate data that can be manipulated by a computer. Sometimes abbreviated as DAQ, data acquisition typically involves acquisition of signals and waveforms and processing the signals to obtain desired information. The components of the data acquisition systems include appropriate sensors that convert any measurement parameter to an electrical signal, which is acquired by the data acquisition hardware.

Diagram 4.1: Stress-Strain Analyser that was used for the determination of polymerization shrinkage force light polymerizable composites.



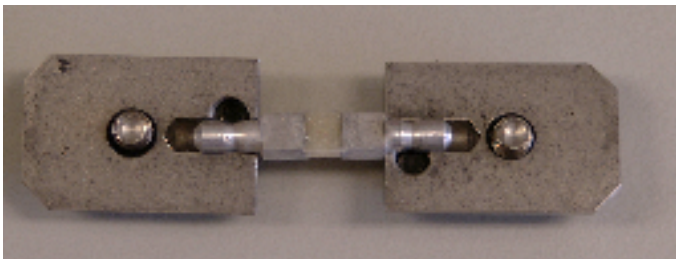


Basic tools required for the experiment

The composite can be placed in such a way that the light initiates the curing and starts the measurements via the photo-diode. The load sensor and the piezo actuator have aluminium attachments which act as bonding surfaces for the composites. The configuration used in this experiment is a simulated

cavity size of 4*4*2 mm^3 which represents a single layer for a typical premolar cavity.

Diagram 4.2: Composite (in the centre) after being polymerized between the prepared surfaces of the aluminium attachments.



The whole unit shown above is the removable part of the platform in the Stress strain analyser, the counterpart of which is the immovable and is the actual mold space for the composite. This picture demonstrates the configuration of the set composite.

The aluminium surface is prepared with ROCATEC (Rocatector Delta, Serial No. 650680, 3M ESPE, Seefeld, Germany). ROCATEC system is a tribochemical method for silicating surfaces. Tribochemistry involves creating chemical bonds by applying mechanical energy. There is no application of heat or light. This is also called ‘cold silicatisation’ because the mechanical energy is transferred to the substrate in the form of kinetic energy and silicatisation takes place macroscopically without change in temperature. The system consists of

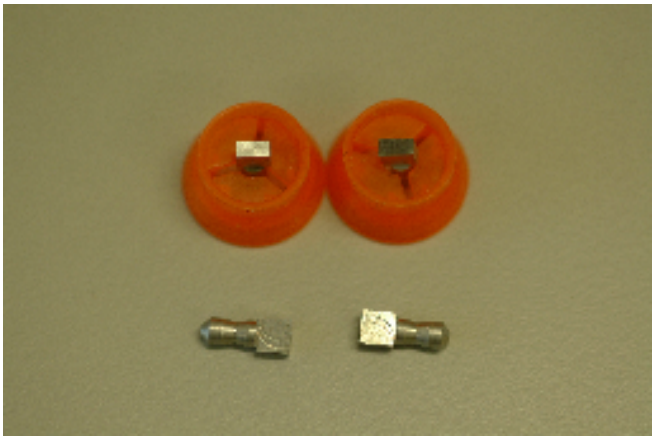
1. A coating unit

2. A micro blasting sand–Rocatec PRE (High purity Al_2O_3 110 µm)

3. Coating sand-Rocatec PLUS or SOFT. (PLUS-High purity Al_2O_3 110 µm, modified with silica; SOFT-High purity Al_2O_3 30 µm, modified with silica)

4. Silane solution-Silane in ethanol; 3M ESPE Sil (resin primer)

Diagram 4.3: The attachment on the left represents the unprepared (shiny) aluminium attachment. The attachment on the right is a Rocatec prepared (dull) attachment.



The steps involved in the preparation of the sample surfaces are micro blasting with PRE to create micro retentive roughness and tribochemical coating with PLUS. Ceramisation of the blasted surface takes place. The affected surfaces of the substrate and grit in the atomic and molecular ranges are excited to such an extent that a so-called TRIBOPLASMA forms. A silane coupling agent, ESPE-Sil, was used (3M ESPE, Seefeld, Germany) and is allowed to dry for 5 minutes after application onto the aluminium

attachments. To enhance bonding Heliobond (Ivoclar Vivadent, Germany LOT G01814) was used to wet and protect the adhesive surface. As the composite needs free and bonded surfaces to simulate a dental cavity, a non-adhesive plastic mold was used between the aluminium attachments. In order to reduce the effects of friction during the polymerization shrinkage process a non-adhesive PTFE tape was adapted to the walls of the simulated cavity. The configuration factor (C-factor) was calculated to be 0.33 (Feilzer *et al,* 1987a). The piezo-actuator served to compensate the compliance of the set up. Compliance means displacement produced per unit force. It is the reciprocal of stiffness. The compliance of the whole test setup including the load cell and the aluminium attachments was determined to be 0.064µm/N (Dullin, 1998). The composite was placed in this mold and covered by a matrix-strip in order to prevent air inhibition and to shape the surface. The types of curing units, the different regimes and the manufacturer details and material properties are presented in the Table 4.1 and Table 4.2

Table 4.1: Details of the light curing units used in the study.

Light curing units	**Manufactures**	**Type**	**Regimes**	**Exposure times**	**Light intensity (mW/cm²)**	**Tip(mm)**
Astralis10 Serial No:013336	Ivoclar Vivadent Schaan, FL	QTH	HIP	10, 20, 40 s	~1200 (1857)*	8
Bluephase Serial No: P0000023	Ivoclar Vivadent Schaan, FL	LED	HIP	10, 20, 40 s	~1100 (1435)*	8
MiniL.E.D Serial No:114-6064	Satelec, Chateau de Tarailhan, France	LED	Fast mode	10, 20, 40 s	~1100 (1141)*	7.5
			Pulse mode	10, 20, 40 pulses		
			Ramping mode	20 s		

* Values in the brackets are light intensity measurements obtained using a thermal sensor

Table 4.2: Material characteristics of the composites used in the study.

Material qualities	Tetric Ceram	Tetric Evo Ceram	Venus	Filtek Supreme
Type	Micro hybrid	Nanohybrid, Nano-optimised mouldable ceramic(Ceromers)	Micro hybrid	Nanocomposite
Organic matrix	Bis GMA,UDMA, TEGDMA	Dimethacrylates, prepolymers,	Bis GMA, TEGDMA	Bis-GMA, UDMA, Bis EMA,TEGDMA
Inorganic	Barium glass, Barium aluminofluoro silicate glass, Ytterbium trifluoride silica, spheroidal mixed oxide.	Barium glass, Ytterbium trifluoride, mixed oxide.	Barium alumino boron, fluoride silica glass, dispersed silicon dioxide.	Silica-nanosilica Zirconia/silica Nanoclusters
Filler particle size	0,7 to 3,0 /1,0 μm	0,4 to 0,7 μm; 10 to 70 nm max.	0,7 μm	20 nm- Nanosilica filler; 5-20 nm Aggregated zirconia/silica; 0,6 - 1,4 μm clusters
Percentage of filler	79 % (wt); 63,7% (vol)	82-83 % (wt); 68% (vol)	78 % (wt); 61% (vol)	78,5 % (wt); 59% (vol)
Manufacturer	Ivoclar Vivadent, Schaan, FL	Ivoclar Vivadent, Schaan, FL	Heraeus Kulzer, Hanau, Ger	3M ESPE, U.S

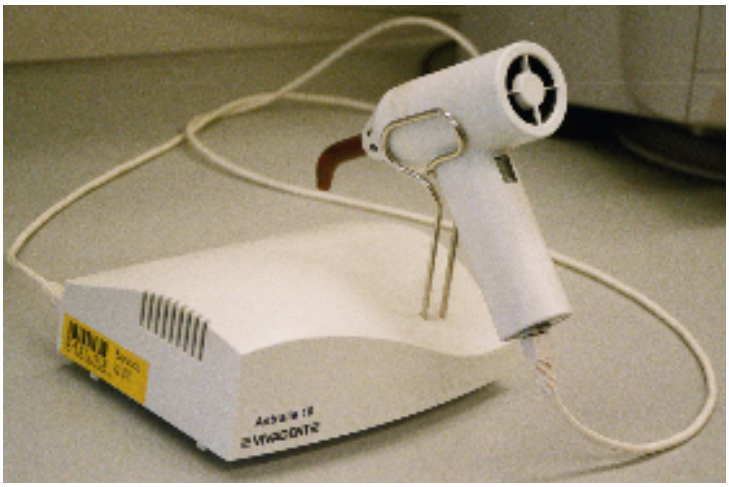
General properties of the lamps:

Astralis 10: Astralis 10 is a high intensity quartz tungsten halogen lamp. The various programmes that are available with this LCU are

- HIP (High Power Program - light intensity of 1200 mW/cm2)
- Adh (Adhesive Program - light intensity of 650 mW/cm2)
- PUL (Pulse Program)
- ECS (Esthetic Cementation System - 30 seconds at 1200 mW/cm.

The above said information is according to the manufacturer.

Diagram 4.4: Astralis 10



Bluephase: Bluephase is a light curing unit which used the light emitting diode technology (LED). It covers a wavelength of 430 to 490 nm.

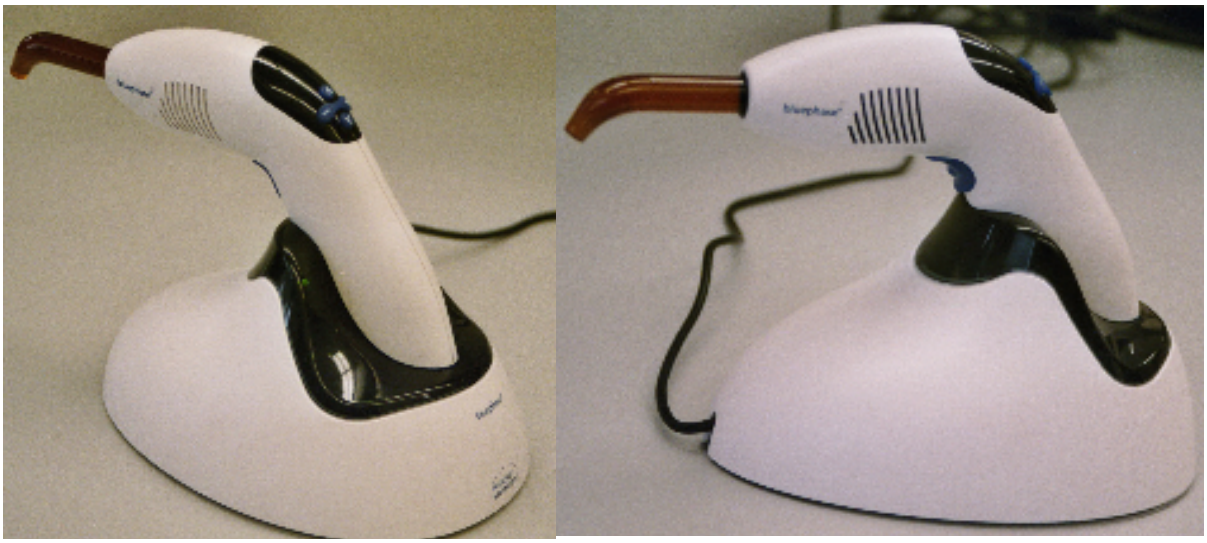


Diagram 4.5: Bluephase

MiniL.E.D: Three different kinds of programs are incorporated by the manufacturer in the MiniL.E.D. They are the

1:**"Fast" mode**: Emits light for 10 seconds at full power.
2:**"Pulse" mode**: Emits 10 successive one-second flashes of light at full power.
3:**"Ramping" mode**: Emits light with gradually increasing intensity (from low power to full power) over a period of 20 seconds.

Fast mode is the normal mode. In the Pulse mode, pulses of light are emitted in such a way that 10 pulses consists of a total of 12 s exposure, 20 pulses comprises of 24 s exposure and 40 pulses have 48 s exposure from the curing unit. The Ramping mode is a programmed mode for 20 s exposure. In this mode the power intensity is low up to the first 10 s after which the intensity rises and remains at the maximum for another 10 s.

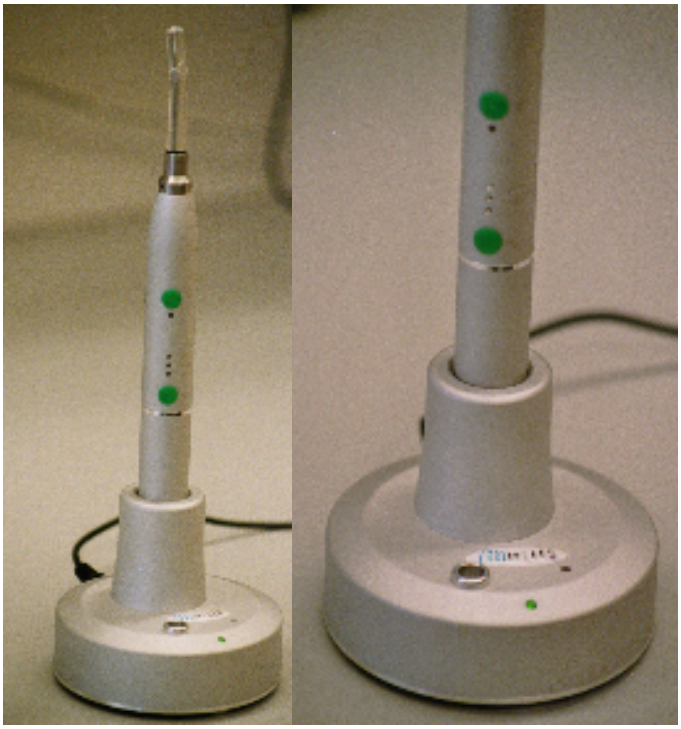
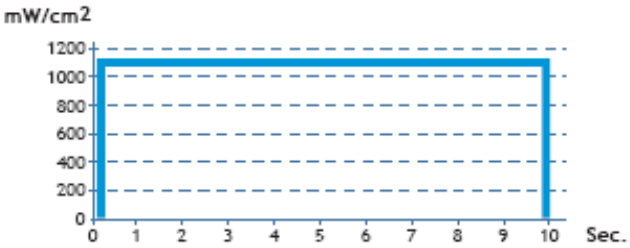
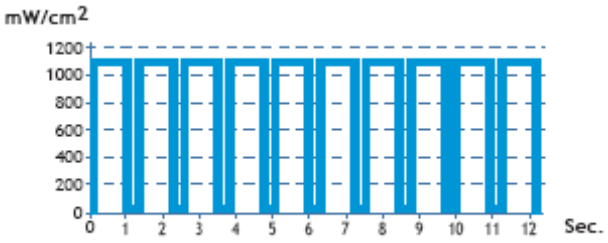


Diagram 4.6: MiniL.E.D

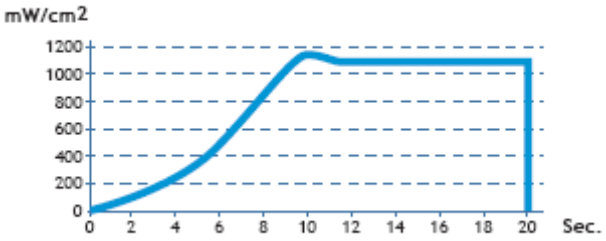
Fast mode



Pulse mode



Ramping mode

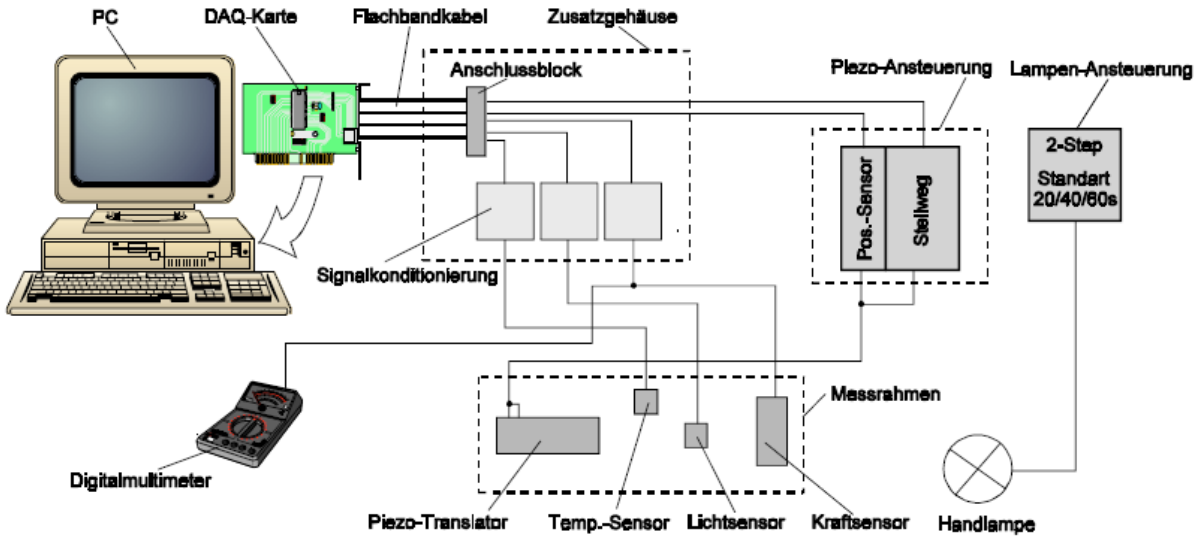


The high intensity halogen lamp, Astralis 10, was used to compare the values with a high intensity light emitting diode curing unit, Bluephase. Since Astralis 10 has high power density it was recommended by the manufacturer that it can cure the composites in 10 s although the golden standard is 40 s. So in this investigation 10 s, 20 s and 40 s exposure times were chosen. Also the HIP was used because it offers the highest intensity and wide spectrum which defines the optimum reference value for the final mechanical data. The comparison of all other light curing units can be made with this reference. In order to compare two light emitting diodes, another LED curing unit namely MiniL.E.D was added to the regime.

Stress Strain Analyser can be used with or without compensation for the compliance of the machine. With compensation of the compliance, the distance between the two aluminium attachments is kept constant by a closed feedback loop between the piezoactuator and the load cell. This means that the actuator is used with a position sensor which provides feedback to the position servo controller compensating for the non-linearity, hysteresis and creep. The real–time force values can be measured by incorporating the compliance into the whole system. Data acquisition was used. The contraction force (N) generated by polymerizing the composite was continuously measured, with compensation and recorded for 300 s after photo-initiation. Each experiment was conducted at room temperature (21–24°C) and the number of samples was eight per group. The maximum contraction stresses after 300 s were computed. From the force values that were obtained, the polymerization contraction stresses [MPa] were calculated. An arbitrary value for the gel–point was also calculated. In this experiment, the time at which the force reaches 0.5 N is considered as an

indirect measure of the gel point. This is the value obtained when the noise level from the machine is multiplied by a factor of ten. The measuring software used was LABVIEW 5.0 which is a graphical programming system for Data Acquisition, measuring unit controls, data analysis and presentation.

Diagram 4.7 : Schematic representation of the Stress Strain Analyser

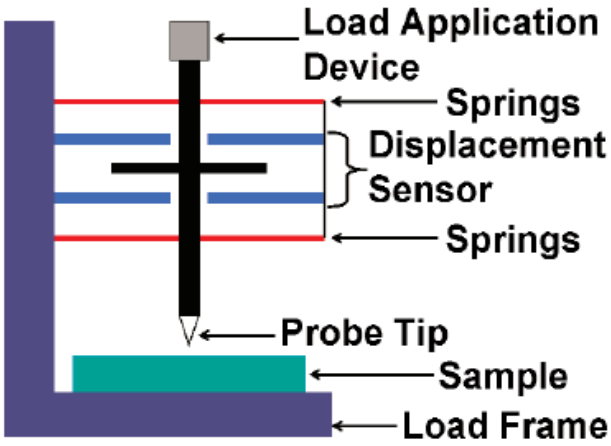


(Courtesy: Dullin, 1998)

The samples along with the attachments were removed from the test system and were used for the measurements of the mechanical properties. The mechanical properties like the micro hardness and modulus of elasticity were measured on these samples with the help of an automatic micro indenter (Fischerscope H100C, No: SNO10001149, Helmut Fischer GmbH, Sindelfingen Germany) immediately after the shrinkage force measurements. Test load range from 0.4 mN to 1000 mN. WIN-HCU software (Helmut Fischer GmbH, Sindelfingen Germany) was used for calculating the mechanical properties. Mechanical properties of both the top and bottom surfaces were measured.

Instrumented indentation testing follows the standards of ISO 14577. The indentation test can be controlled either in force or depth. The test can be a macro, micro or nano range test based on the following force and depth criterion (www.csm-instruments.com).

Diagram 4.8: Schematic representation of an instrumented indentation system



i. Macro range: 2 N < F < 30 kN

ii. Micro range: 2 N > F; h > 200 nm

iii. Nano range: h < 200 nm.

The Fischerscope measures the

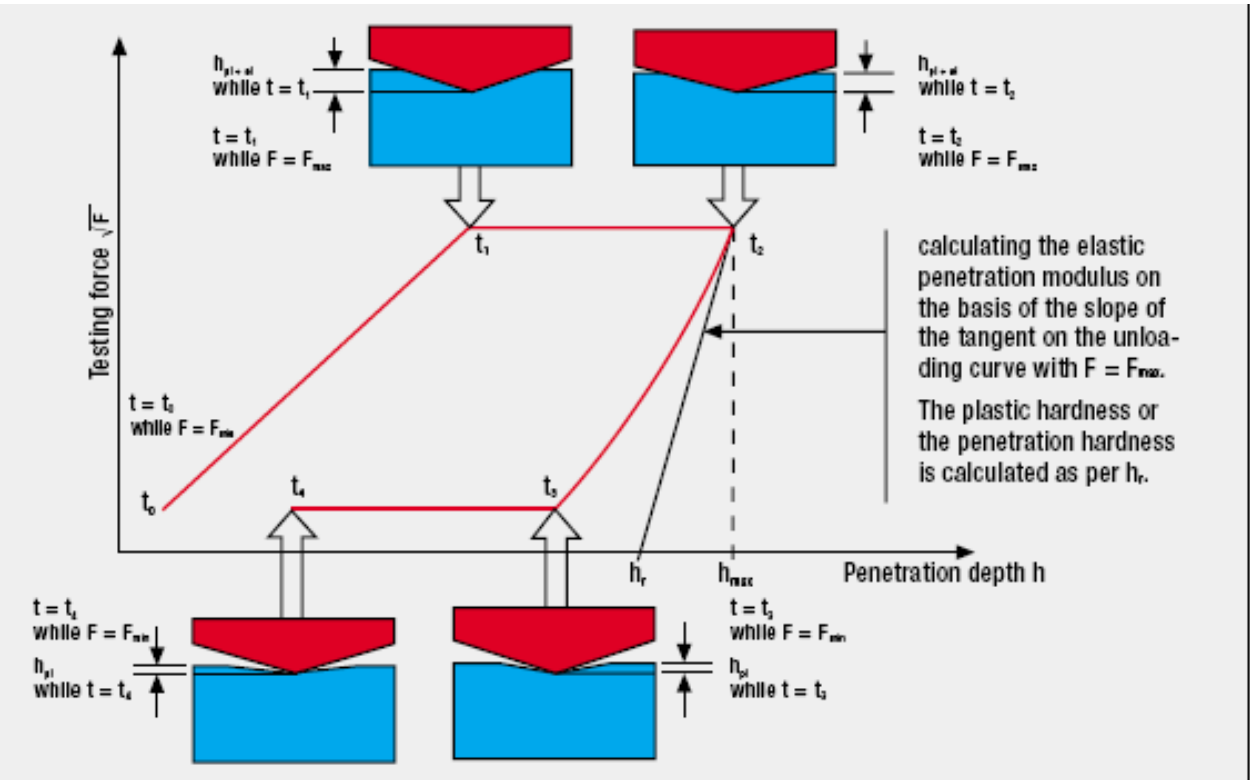
a. Martens Hardness (Universal Hardness) HM. Martens Hardness is defined as the maximum applied load, F_{max} divided by the contact area (A) at the load.

$$HM= F_{max} /A$$

b. Indentation Modulus (E_{IT}): The indentation modulus is calculated from the slope of the tangent of the unloading curve, using a linear fit to the initial unloading data or a power-law fit.

c. Indentation Creep: Indentation creep can be defined as the relative change of the indentation depth whilst the applied load remains constant.

Diagram 4.9: An indentation force-displacement curve in which several important parameters are illustrated.



Statistical analyses were done using One-way-ANOVA ($p<0.05$) and Tukey post-hoc test. The SPSS 12.0 version software (SPSS Inc, Chicago, IL) was used for the same.

Chapter 5

Influence of distance of the light source on the polymerisation shrinkage stress and mechanical properties.

Introduction: Distance of the light source from the composite has always been a topic of discussion. Most of the studies recommend the closest distance possible to be applied while photo polymerising the resin composite. The major factor considered in the studies was based on the mechanical properties such as hardness. Few studies explain the influence of distance on the contraction stress. The contraction stress is influenced by the distance of the light source, the diameter of the tip of the source, exposure time and light intensity. The physical properties can be modified based on the total energy delivered to the composite and may not be dependent on the variables like exposure time or distance independently (Abate *et al,* 2001)

Objective: Since decreasing the stress levels is also one of the major concerns in improving the material behaviour, we studied the influence of distance of the light source on the polymerisation shrinkage stress and mechanical properties with two modern curing units namely Astralis 10 and Bluephase for 10 s.

Material and methods: Tetric Ceram, the universal micro hybrid composite with A3 shade (LOT NO: D54812) was used. The determination of mechanical properties was done immediately after the shrinkage force measurements. Astralis 10 and Bluephase light curing units were used for 10s.

Distances of 0,1,2,3 and 6mm from the composite top surface were used to polymerise the composite. Top surface is the surface that is directly exposed to the light. Bottom surface is the surface which is 2mm away from the top surface because the thickness of each composite is 2mm.

Results: The data from the experiments are tabulated in Table 5.1 and Table 5.2

Table 5.1: Shrinkage force, shrinkage stress and the gel point attained by curing Tetric Ceram using Astralis 10 (QTH) and Bluephase (LED) for 10 s at various distances. The stress is high for Astralis 10 at 1mm correspondingly; the gel point is low which gives a definite correlation.

Light curing units	Distances [mm]	Force [N]	Stress [MPa]	Gel point [s]
Astralis 10 (10 s)	0	23,8 (5,4) $^{a, b, c}$	2,9(0,6) ^{d}	3,0 (0,9)$^{a, b, c}$
	1	27,5 (3,3) ^{a}	3,4 (0,4) ^{d}	2,5 (0,2)^{a}
	2	23,5 (3,0) $^{a, b}$	2,9 (0,3) ^{d}	2,7 (0,5)$^{a, b}$
	3	20,7 (3,4) $^{a, b, c}$	2,5 (0,4) ^{b,c,d}	3,0 (0,4)$^{a, b, c}$
	6	12,8 (0,7) $^{a, b, c}$	1,6 (0,1) ^{a}	3,2 (1,3)$^{a, b, c}$
Bluephase (10 s)	0	22,2 (3,4) ^{a}	2,7 (0,4) ^{c,d}	2,2 (1,1)^{a}
	1	21,3 (1,8) $^{a, b, c}$	2,6 (0,2) ^{b,c,d}	2,9 (0,2)$^{a, b, c}$
	2	15,3 (7,1) $^{b, c}$	1,9 (0,8) ^{a,b,c}	4,6 (1,8)$^{b, c}$
	3	14,0 (2,6) $^{a, b, c}$	1,7 (0,3) ^{a,b}	3,6 (0,8)$^{a, b, c}$
	6	11,1 (0,6) ^{c}	1,3 (0,1) ^{a}	4,8 (0,3)^{c}

Table 5.2: Hardness values and modulus of elasticity at the top and bottom of the sample immediately after curing and shrinkage force measurements. The highest hardness and modulus of elasticity values were obtained by Astralis 10 at 1mm.

Light curing units	Distance [mm]	Vickers Hardness- [HV] TOP	Vickers Hardness- [HV] BOTTOM*	Modulus of elasticity [GPa] TOP	Modulus of elasticity [GPa] BOTTOM*
Astralis10 (10 s)	0	44,0(9,0) ^{a,b,c}	23,0 (12,0) ^{a,b,c}	9,0 (1,4) ^{b,c}	6,5 (2,0) ^{b,c,d}
	1	52,0(10,5) ^{c}	35,5 (14,0) ^{d}	9,4 (1,2) ^{c}	8,2 (1,6) ^{e}
	2	43,3 (9,9) ^{a,b}	30,2 (11,5) ^{c,d}	8,8 (1,9) ^{b,c}	7,6 (1,4) ^{c,d,e}
	3	48,2 (8,8) ^{b,c}	28,2 (10,2) ^{b,c,d}	9,1 (1,4) ^{b,c}	7,1 (1,7) ^{b,c,d,e}
	6	42,3 (8,1) ^{a,b}	15,0 (4,6) ^{a}	8,3 (0,7) ^{a,b,c}	4,7 (1,0) ^{a}
Bluephase (10 s)	0	44,0(8,4) ^{a,b,c}	35,1 (12,4) ^{d}	9,0 (1,1) ^{b,c}	8,0 (2,4) ^{d,e}
	1	47,0(8,6) ^{a,b,c}	30,5 (8,9) ^{c,d}	9,0 (1,1) ^{b,c}	8,1 (1,5) ^{d,e}
	2	39,3 (10,5) ^{a}	22,2 (10,6) ^{a,b,c}	7,3 (1,3) ^{a}	6,0 (2,3) ^{a,b,c}
	3	41,0(10,1) ^{a,b}	20,0 (4,3) ^{a,b}	8,0 (1,2) ^{a,b}	6,0 (1,0) ^{a,b,c}
	6	39,0 (3,5) ^{a}	15,6 (5,2) ^{a}	8,0 (0,6) ^{a,b}	5,6 (1,4) ^{a,b}

*BOTTOM surface indicates the surface that is 2mm away from the top surface.

Figure 5.1: Comparison of shrinkage stress values between Astralis 10 and Bluephase for distances 0, 1, 2, 3 and 6mm.

X-axis: represents the two lamps at various distances A0=Astralis10 at 0mm; A1= Astralis10 at 1mm; A2= Astralis 10 at 2mm; A3= Astralis 10 at 3mm and A6= Astralis 10 at 6mm.B0= Bluephase at 0mm; B1= Bluephase at 1mm; B2=Bluephase at 2mm; B3=Bluephase at 3mm and B6= Bluephase at 6mm. Y axis represents the shrinkage stress in MPa.

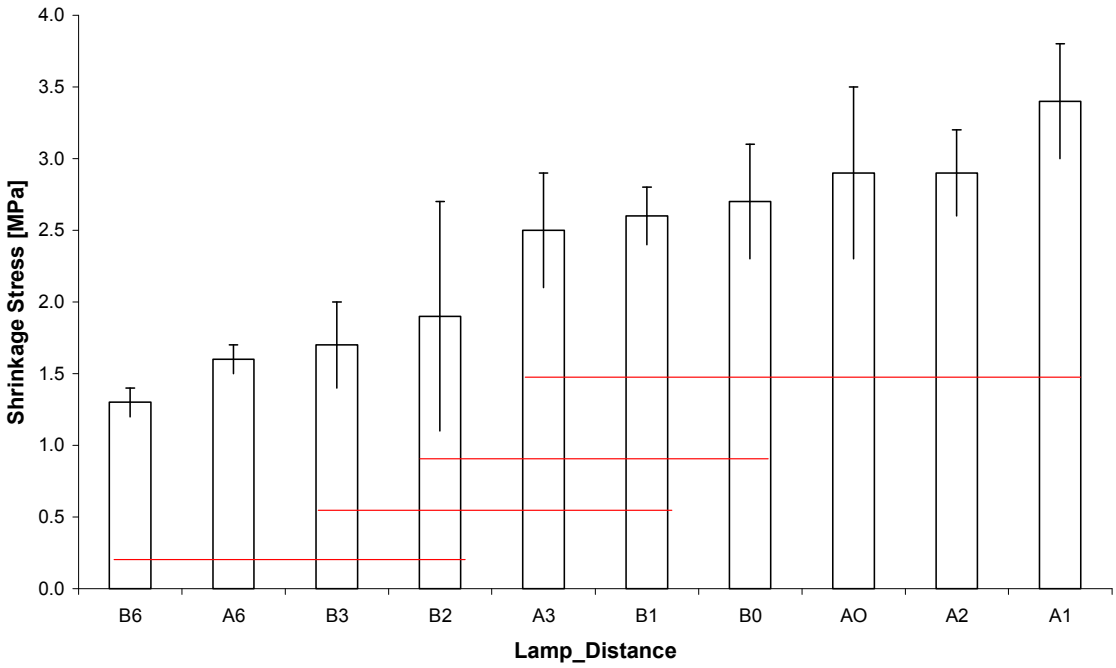


Figure 5.2: Gel point as achieved during the curing of Tetric Ceram at various distances.

Lamp_Distance represents A0=Astralis10 at 0mm; A1= Astralis10 at 1mm; A2= Astralis 10 at 2mm; A3= Astralis 10 at 3mm and A6= Astralis 10 at 6mm.B0= Bluephase at 0mm; B1= Bluephase at 1mm; B2=Bluephase at 2mm; B3=Bluephase at 3mm and B6= Bluephase at 6mm. Y axis represents the Gel point in seconds.

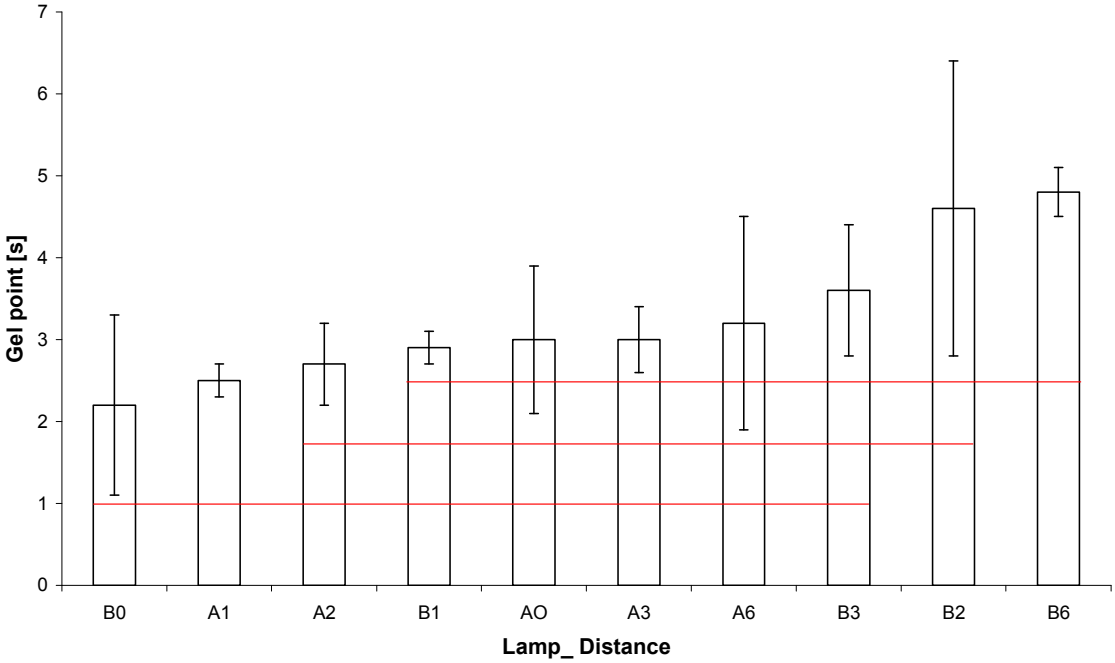


Figure 5.3: The top and bottom hardness values (HV) of Tetric Ceram at various distances.

Lamp_Distance represents A0=Astralis10 at 0mm; A1= Astralis10 at 1mm; A2= Astralis 10 at 2mm; A3= Astralis 10 at 3mm and A6= Astralis 10 at 6mm.B0= Bluephase at 0mm; B1= Bluephase at 1mm; B2=Bluephase at 2mm; B3=Bluephase at 3mm and B6= Bluephase at 6mm. Y axis represents the shrinkage stress in MPa. The highest HV that was reached by the composite Astralis 10 at 1mm distance is taken as a reference value and is considered to the 100% that is achievable based on which the 80% cut-off for the bottom surface are derived for all the group. Thick line denotes 100% HV; Dotted line denotes 80% HV. These values do not indicate the post curing hardness values.

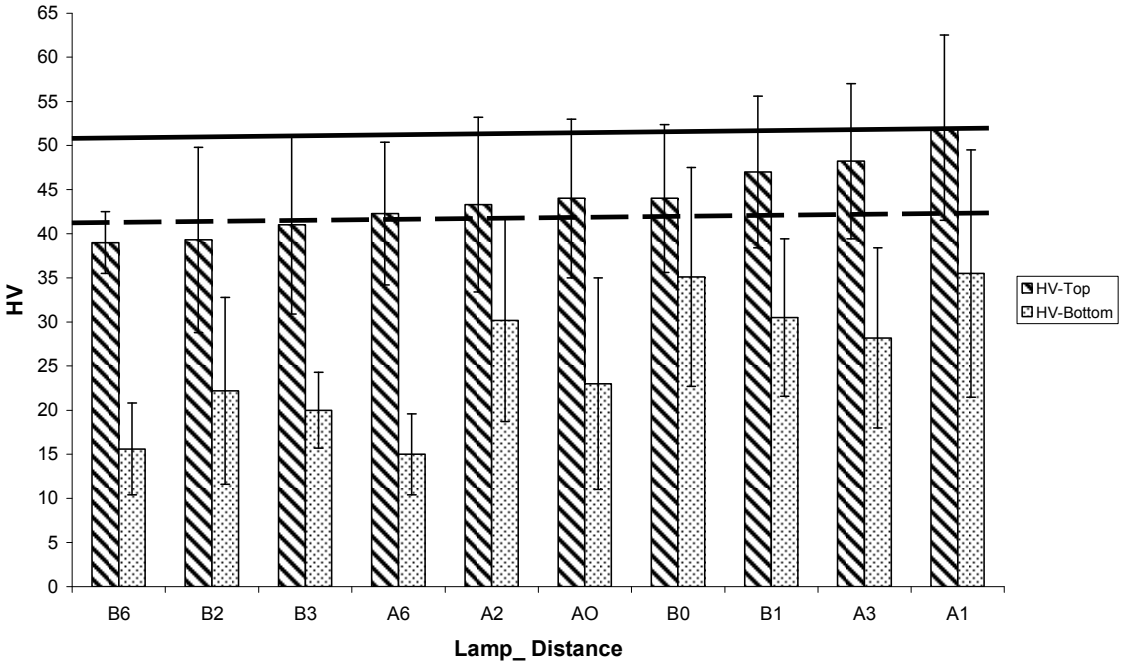
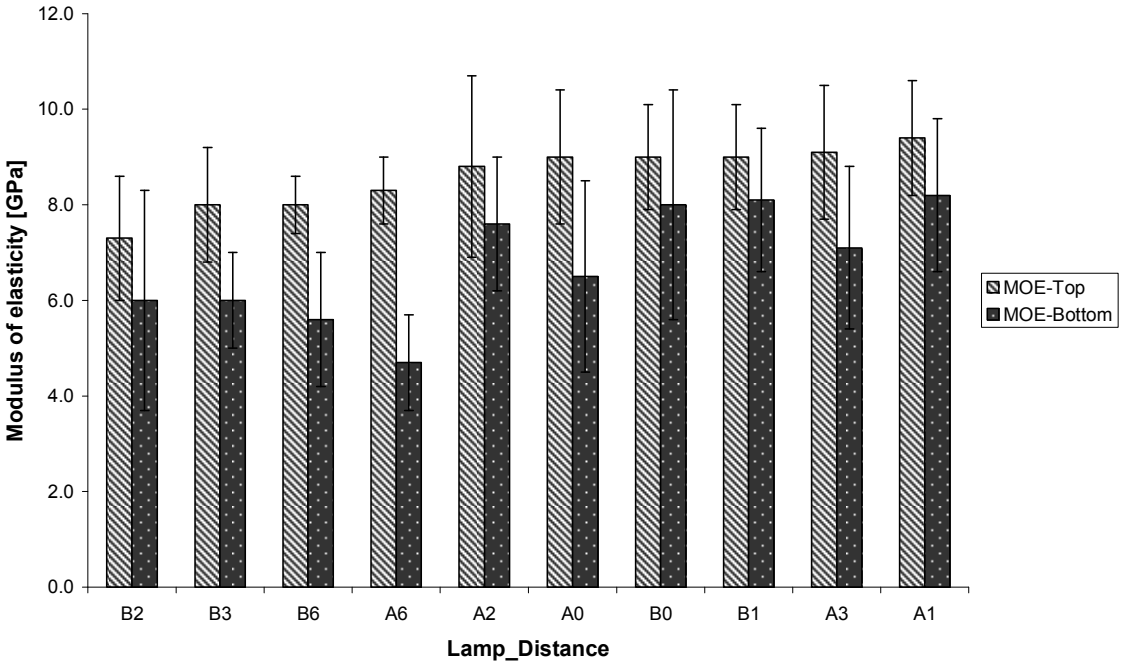


Figure 5.4: Top and bottom modulus of elasticity (MOE) for distances of 0, 1, 2, 3 and 6mm for Astralis 10 and Bluephase at 10 s. Lamp_Distance represents A0=Astralis10 at 0mm; A1= Astralis10 at 1mm; A2= Astralis 10 at 2mm; A3= Astralis 10 at 3mm and A6= Astralis 10 at 6mm.B0= Bluephase at 0mm; B1= Bluephase at 1mm; B2=Bluephase at 2mm; B3=Bluephase at 3mm and B6= Bluephase at 6mm.



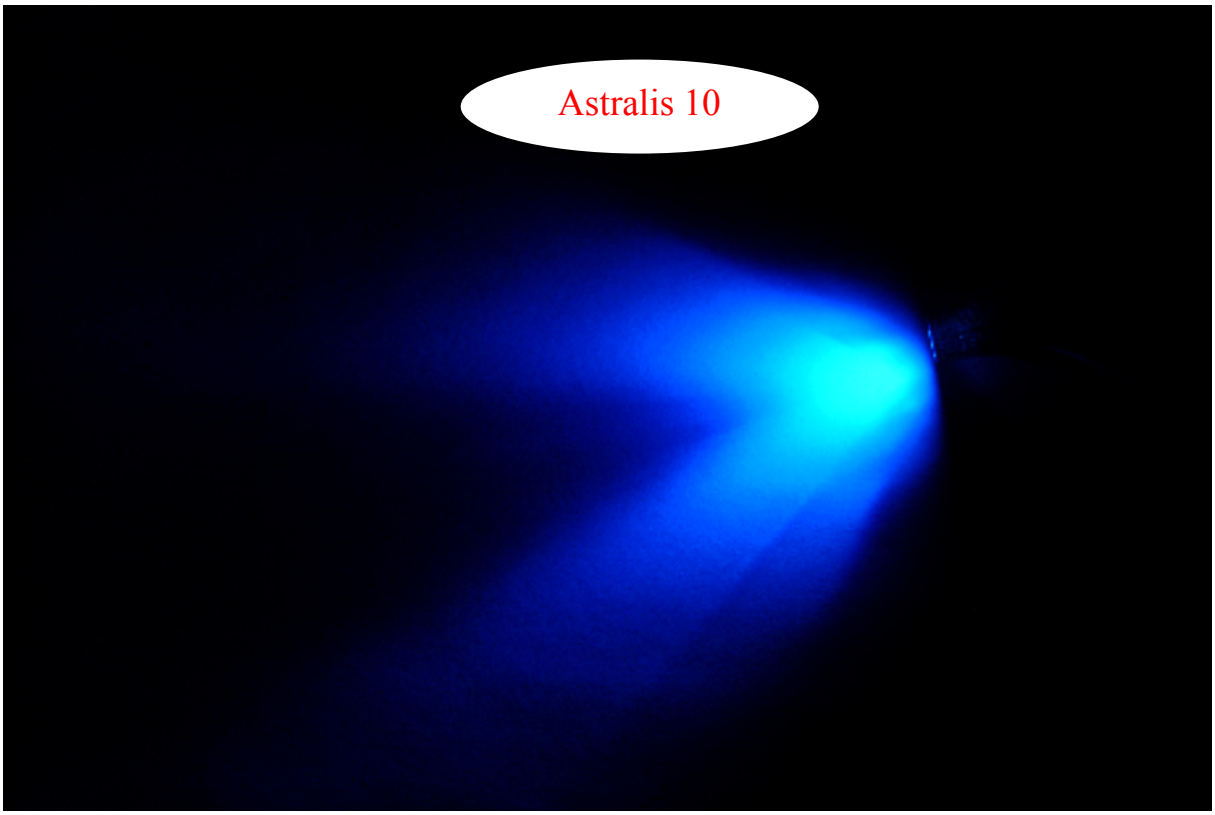
Discussion:

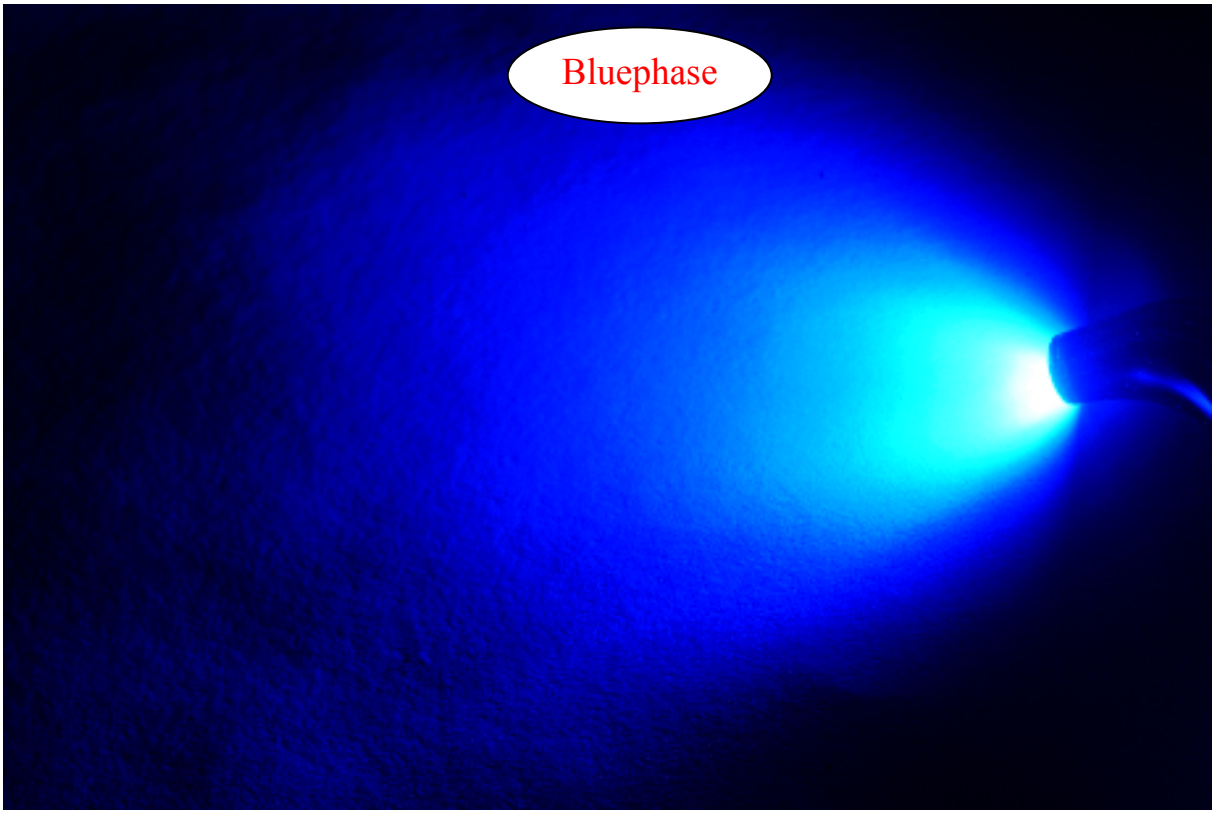
From the figures, it is evident that at a distance of 1mm from the top of the resin sample, the stress and the hardness values are high. The gel point is inversely proportional to the contraction stress. A high contraction stress has developed because the material has little time to flow and has gained rigidity soon. This is more prominent when cured with the very high intensity light curing units like Astralis 10. In a study conducted by Murchison and Moore, it was shown that hardness of resin liners was better at a distance of 3mm from the cavity floor than at 0mm or 6mm (Murchison and Moore, 1992).

While trying to find out the reason as to why at a distance of 1mm should the stress as well as the hardness be higher (though not statistically significant from 0mm), we found that it could be rendered to the

1. The influence of the turbo-tip and the convergence of the light rays.
2. The high temperature or heat dissipated by the high intensity Astralis 10.

Though the Bluephase also has a turbo-tip this effect is not evident because the heat produced is not as high as that of Astralis 10. At this point it is useful to compare as to how the light rays emerge from the tip of the light guide for the two light curing units.





There is a difference in the emergence of light between the two LCU. This is one major contributing feature as the curing light / tip combination that delivers the greatest total energy produce the hardest specimens (Price *et al,* 2003).Commonly, heat is measured with a thermal sensor which measures the heat of the light and the exothermal energy.

From the Fig V- 3, it is evident that none of the combination of light and distance produced a properly cured composite based on the hardness values at the bottom (except Bluephase 10 s which produced 79.5% bottom hardness) The dictum that the bottom surface should have 80% of the hardness of the top surface in order to become a properly cured material is not achieved.

This can be due to two possible reasons

1. Lack of post curing as all composite samples were subject to immediate hardness tests rather than after post curing.
2. Only a 10 s exposure time was used in the experiment which has possibly been not able to produce a sufficiently cured composite.

A good correlation between HV and modulus of elasticity can be visualised from the graphs in the Fig.V-3 and V-4. The hardness and modulus of elasticity go hand in hand for both Astralis 10 and Bluephase for almost all the distances. This indicates that the materials with high rigidity also have high hardness. Hardness and modulus of elasticity are high for a distance of 1mm for both the light curing units. Then there is a difference in the pattern. For Astralis 10, increasing the distance up to 3mm increases both the mechanical properties whereas for Bluephase decreasing the distance has resulted in better mechanical properties, though these values are not statistically significant. The light guide has a much big role to play in increasing or decreasing the mechanical properties. One more aspect is that the tip of the light source at 0mm, 2mm and 6mm is not warm enough when compared to 1mm and 3mm. As the light rays are guided to emerge there is some dissipation of warmth at certain intervals which in this case can be considered as 1mm. Periods of high and low heat gives us the idea that the energy is concentrated in pockets. Both the LCU have this tendency but is more pronounced in Astralis 10.

Conclusion: Polymerisation stress is a more sensitive indirect parameter to determine the curing quality than hardness value based on its statistical discrimination power. For a curing depth of 2mm, post curing should be relied to achieve proper cure. Gel point is inversely related to shrinkage stress.

Chapter 6

Influence of curing times and intensity variation on a micro hybrid composite (Tetric Ceram)

Objective: The aim of the study was to understand the shrinkage force patterns and mechanical properties of a micro hybrid composite and to use the data thus obtained to compare with other composite types such as nano composites and nanohybrid.

Material and methods: Tetric Ceram, A3 shade with LOT NO: D22993 was used. This composite will serve as a standard for comparative studies. The study consisted of 13 regimes. The regimes are a combination of the light curing units along with the exposure time and mode of curing. Three different light curing units were studied at 10 s, 20 s and 40 s. Astralis 10, Bluephase and MiniL.E.D were the 3 LCU. Different modes of curing were considered under the LCU, MiniL.E.D. They are the Fast mode, Pulse mode and the Ramping mode. In each mode exposure times of 10 s, 20 s and 40 s were used.

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For easy understanding, the 13 regimes are as follows:

No. of regimes	Regimes
1	Astralis 10 (HIP) for 10 s
2	Astralis 10 (HIP) for 20 s
3	Astralis 10 (HIP)for 40 s
4	Bluephase (HIP) for 10 s
5	Bluephase (HIP) for 20 s
6	Bluephase (HIP) for 40 s
7	MiniL.E.D–Fast mode for 10 s
8	MiniL.E.D–Fast mode for 20 s
9	MiniL.E.D–Fast mode for 40 s
10	MiniL.E.D–Pulse mode for 10 s
11	MiniL.E.D–Pulse mode for 20 s
12	MiniL.E.D–Pulse mode for 40 s
13	MiniL.E.D–Ramping mode for 20 s

Results:

Results are tabulated in the Table 6.1 and Table 6.2 based on which Figures 6.1, 6.2, 6.3, and 6.4 are drawn.

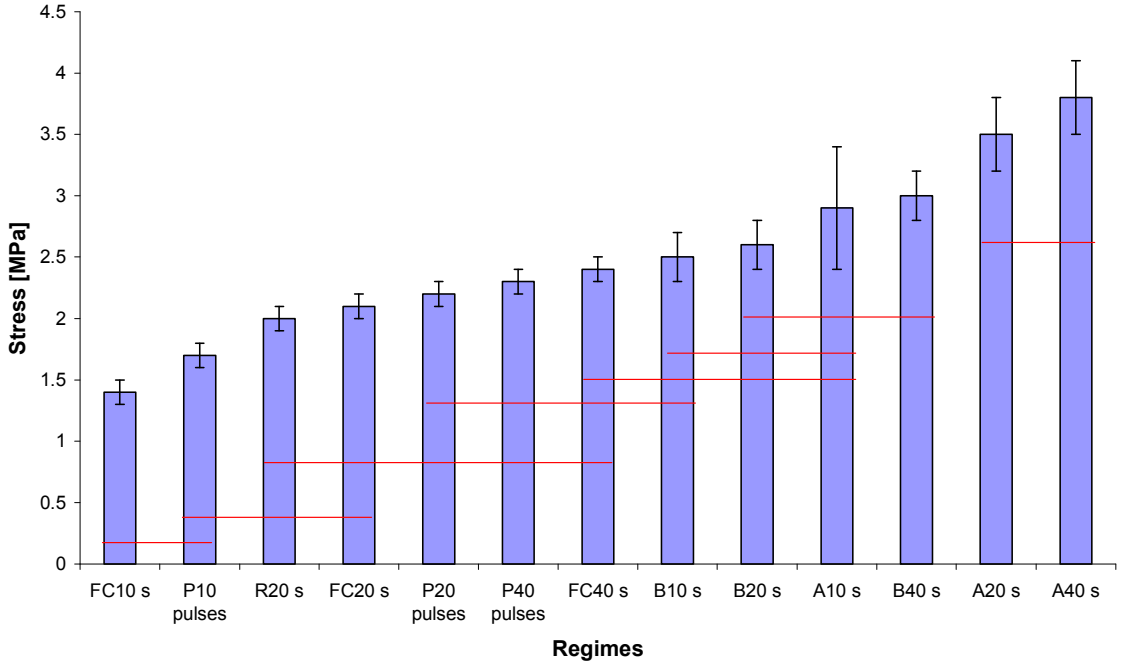
Table 6.1 The stress, gel point and the modulus of elasticity (top and bottom) values for all the thirteen regimes.

LCU	Time	Stress [MPa]	Gel point [s]	Modulus of elasticity(Top)	Modulus of elasticity (Bottom)
Astralis 10	10 s	2,9 (0,5)^{f,g}	2,2 (0,3)^{a}	9,1 (1,3)^{c,d}	7,9 (1,4)^{b,c}
	20 s	3,5 (0,3)^{h}		10,4 (1,5)^{e}	7,8 (2,0)^{b,c}
	40 s	3,8 (0,3)^{h}		9,9 (1,3)^{d,e}	9,7 (1,0)^{d}
Bluephase	10 s	2,5 (0,2)^{d,e,f}	2,2 (0,3)^{a}	8,8 (1,2)^{c,d}	8,6 (2,1)^{c,d}
	20 s	2,6 (0,2)^{e,f,g}		8,4 (1,5)^{b,c}	9,0 (1,3)^{c,d}
	40 s	3,0 (0,2)^{g}		8,2 (1,4)^{b,c}	8,1 (3,5)^{b,c,d}
MiniL.E.D Fast mode	10 s	1,4 (0,1)^{a}	2,8 (0,4)^{b}	7,4 (1,2)^{b}	5,7 (0,8)^{a}
	20 s	2,1 (0,1)^{b,c}		8,3 (0,9)^{b,c}	7,6 (1,2)^{b,c}
	40 s	2,4 (0,1)^{c,d,e}		8,4 (1,0)^{b,c}	7,9 (1,1)^{b,c}
MiniL.E.D Pulse mode	10 pulses	1,7 (0,1)^{a,b}	2,8 (0,3)^{b}	5,9 (0,7)^{a}	6,7 (1,4)^{a,b}
	20 pulses	2,2 (0,1)^{c,d}		7,3 (0,7)^{b}	8,2 (1,4)^{b,c,d}
	40 pulses	2,3 (0,1)^{c,d,e}		8,3 (0,9)^{b,c}	7,7 (1,6)^{b,c}
MiniL.E.D Ramping mode	20 s	2,0 (0,1)^{b,c}	5,6 (0,2)^{c}	7,5 (1,7)^{b}	7,8 (0,8)^{b,c}

Table 6.2: This table explains the hardness values and the percentage of bottom hardness values achieved by all the regimes. % Hardness (B/T)* 100 represents % of the bottom HV of the each regime taking into account the top HV of the corresponding regime. % Hardness (B/58,2)* 100 represents the % of the bottom HV achieved by each regime taking into account the highest HV of all the 13 regimes which is achieved by Astralis 10, 20s at the top .

LCU	Time	HV (Top)	HV (Bottom)	%Hardness (B/T)* 100	%Hardness (B/58,2)* 100
Astralis 10	10 s	45,5 (8,7)^{b}	32,4 (9,3)^{a}	71,2	55,6
	20 s	58,2(12,2)^{c}	51,4 (16,3)^{c}	88,3	88,3
	40 s	49,2 (10,7)^{b,c}	48,9 (11,3)^{b,c}	99,3	84,0
Bluephase	10 s	42,7 (9,5)^{a,b}	38,6 (11,5)^{a,b,c}	90,3	66,3
	20 s	46,7 (17,0)^{b}	47,6 (15,5)^{b,c}	100,1	81,7
	40 s	46,5 (16,0)^{b}	47,6 (26,4)^{b,c}	100.9	81,7
MiniL.E.D Fast mode	10 s	52,7 (18,8)^{b,c}	35,8 (10,2)^{a,b}	67,9	61,5
	20 s	46,2 (9,6)^{b}	39,1 (11,9)^{a,b,c}	84,6	67,1
	40 s	43,6 (5,7)^{b}	41,9 (14,1)^{a,b,c}	96,1	71,9
MiniL.E.D Pulse mode	10 pulses	31,6 (6,5)^{a}	41,2 (16,1) ^{a,b,c}	130,3	70,7
	20 pulses	41,8 (10,1)^{a,b}	40,3 (12,3) ^{a,b,c}	96,4	69,2
	40 pulses	43,8 (8,1)^{b}	38,1 (14,6) ^{a,b,c}	86,9	65,4
MiniL.E.D Ramping mode	20 s	46,2 (12,1)^{b}	37,9 (12,9) ^{a,b,c}	82,0	65,1

Figure 6.1: The polymerization shrinkage stress for all the 13 regimes. Homogenous subsets are marked by linear lines.



A10s= Astralis 10,10s

A20s=Astralis10, 20s

A40s= Astralis10, 40s

B10s=Bluephase, 10s

B20s=Bluephase, 20s

B40s= Bluephase, 40s

FC10s= MiniLED,Fast cure mode, 10s

FC20s=MiniLED, Fast cure mode, 20s

FC40s=MiniLED, Fast cure mode, 40s

P10 pulses=MiniLED, Pulse mode, 10pulses

P20 pulses=MiniLED, Pulse mode, 20 pulses

P40 pulses=MiniLEd, Pulse mode, 40 pulses

R20s=MiniLED, Ramp mode, 20s

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Figure 6.2: Hardness values at the top surface for 20 s for the LCU Astralis 10 (A20) , Bluephase (B20), MiniL.E.D [Fast mode(FC20); Pulse mode (P20); Ramping mode (R20)].

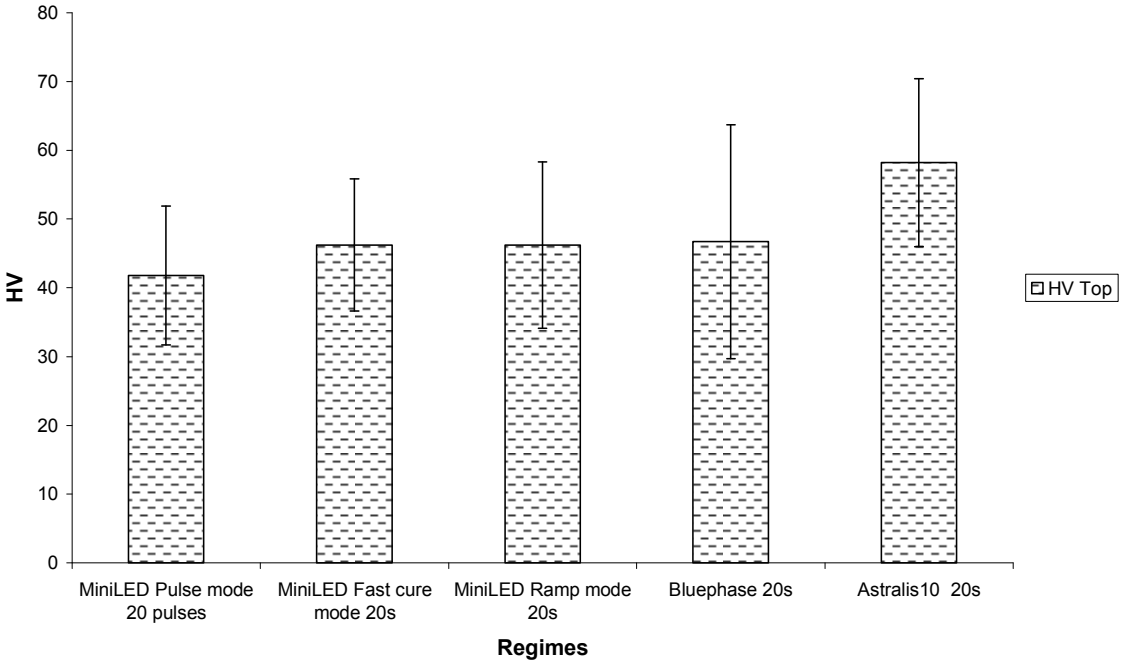


Figure 6.3: The modulus of elasticity follows the same pattern as that of the HV. Astralis 10 produces the highest modulus of elasticity followed by Bluephase and MiniL.E.D.

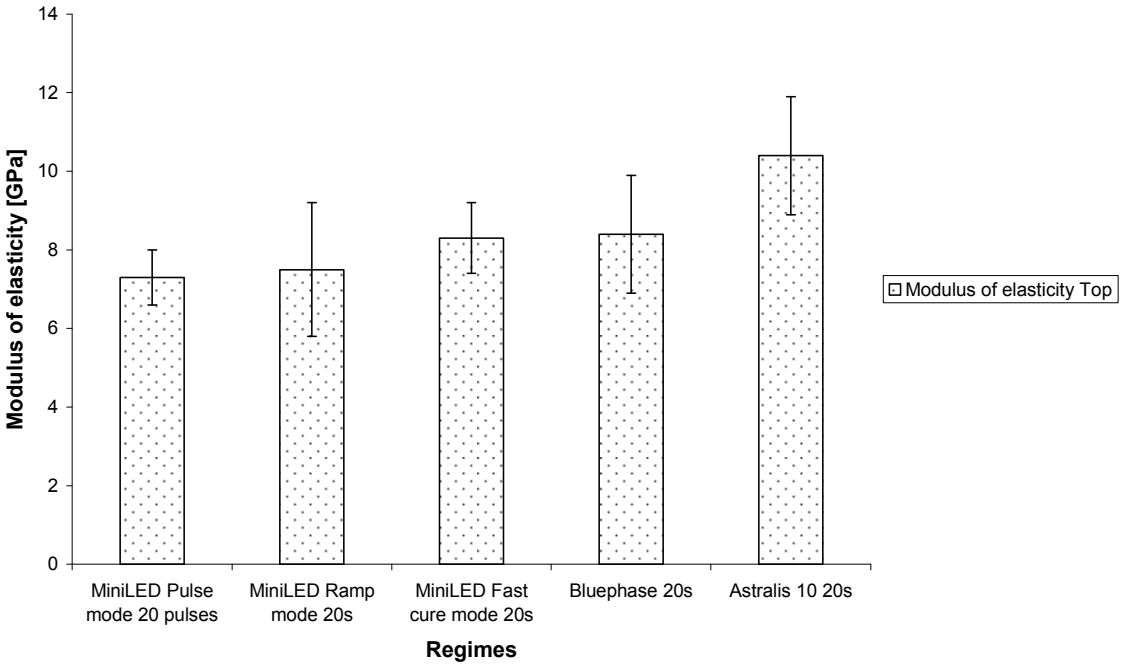
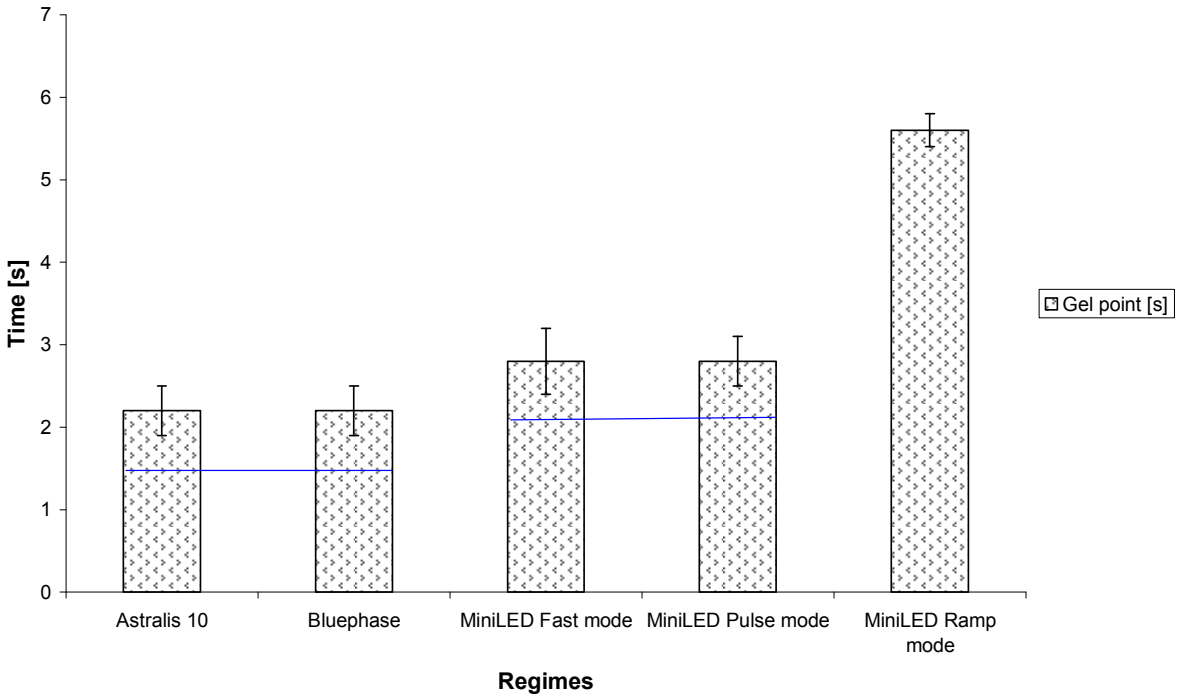


Figure 6.4: Gel point as achieved by the light curing units .



Discussion:

From Table 6.1, the high value for stress is for Astralis10, 40 s. The highest HV was achieved by Astralis 10 20 s. Also the modulus of elasticity value for the top is high for Astralis 10 for 20 s. The longest gel point is for Ramping mode. Gelation is extended when the light intensity is increased gradually. This means Ramping mode hardens the composite a little later (nearly twice as much time as other regimes) than Astralis 10, Bluephase or by the other regimes such as Fast mode and Pulse mode of the curing units. The long gel period also helps in reducing the initial buiding up of the contraction stress. This can be seen in the stress diagram where Ramping mode (which is cured at 20 s) produced the least stress when compared to other curing units at the same exposure time.

The lowest stress value developed for Fast mode at 10 s for MiniL.E.D whereas the highest stress value was recorded by Astralis 10 at 40 s. Fig 6.2 shows that the Hardness Values of the LCU at 20s makes it clear that Astralis 10 produced the hardest composite followed by Bluephase and Mini LED. For the same exposure time, Astralis 10 yield high HV.Considering the situation for bottom hardness most of the regimes have attained 80% hardness as that of top. This can be seen on Table 6.2. But, when the bottom hardness of all the regimes is calculated based on the HV of the Astralis 10 at 20s (which is the highest) then only 4 regimes namely Astralis 10 at (20 s and 40 s) and Bluephase (20 s and 40 s) can be considered to be properly cured material of all the 13 regimes.

Chapter 7

(i): Tetric Evo Ceram- a nano-optimised composite

Objective: Tetric Evo Ceram, according to the manufacturer is a new and improved version of Tetric Ceram with more technology introduced into the formation of the filler particles. Prepolymers are added to the fillers. The aim of the study was to determine the properties of Tetric Evo Ceram.

Material and methods: Tetric Evo Ceram with LOT NO: F38346 and A3 shade was used.

***Table 7.1*:** Light curing units, regimes, exposure times, and the light intensities that were used in this experiment.

Light curing units	Manufactures	Type	Regimes	Light intensity (mW/cm^2)	Tip(mm)	Exposure times(s)
Astralis10 Serial No:013336	Ivoclar Vivadent Schaan, FL	QTH	HIP	1857	8	10, 20, 40
Bluephase Serial No: P0000023	Ivoclar Vivadent Schaan, FL	LED	HIP	1435	8	10, 20, 40
MiniL.E.D Serial No:114-6064	Satelec, Chateau de Tarailhan, France	LED	Fast mode	1141	7.5	10, 20, 40
			Pulse mode			10, 20, 40
			Ramping mode			20

Results: Results are shown on Tables 7.2, 7.3 and 7.4.After analysing the data, statistics reveals significant differences in the polymerization shrinkage stress of Tetric Evo Ceram for 10 s, 20 s and 40 s polymerization using Astralis 10 LCU. The lowest stress values were recorded for the Fast mode 10 s and Pulse mode 10 s programs of the MiniL.E.D whereas the Astralis10 at 40 s polymerized the composite producing high stress The modulus of elasticity is high after curing the composite with Astralis10 at 10 s, 20 s, 40 s and the Bluephase for 40 s. The lowest moduli of elasticity were recorded

for the Fast, Pulse and Ramping modes of MiniL.E.D and for the Bluephase 20 s and 10 s.

The hardness values also followed the same pattern as the modulus of elasticity.

The composite gelates slowly when cured using the Ramping mode (7.5 s) of the MiniL.E.D. The gel points remain the same for the other regimes regardless of the exposure times. No statistical differences could be found among the gel points achieved by Astralis 10, Bluephase and the MiniL.E.D except for the Ramping mode.

The details of the results are presented in Table7.2 and 7.3. Table 7.4 shows the correlation among polymerization shrinkage stress, gel point, modulus of elasticity (E) and the hardness values (HV).

***Table 7.2*:** The polymerization shrinkage stress, gel point, the Vickers Hardness and the Modulus of Elasticity (E) values of the different regimes of the curing units. Homogenous subsets within a light curing unit are represented by similar superscripts. The standard deviations are represented within the parentheses.

Regimes	Time	Stress [MPa]	Gel Point [s]	Hardness[HV]		% Hardness (#)	% Hardness (# #)
				Top	Bottom		
Astralis 10	10 s	2,7 (0.3) ^{e}	2,3(0.3)^{a}	57,7 (14,1) ^{e}	28,7 (9,8) $^{a, b}$	49,7	48,6
Astralis 10	20 s	3,4 (0.3) ^{f}		50,9 (18,6) $^{e, d}$	29,0 (16,9) $^{a, b}$	56,9	49,1
Astralis 10	40 s	3,8 (0.3) ^{g}		59,0 (21,4) ^{e}	34,4 (16,8) ^{b}	58,3	58,3
Bluephase	10 s	1,6(0.1)^{c}	3,7(0.4)^{b}	48,4 (7,4) $^{b, c, d}$	21,8 (11,2) ^{a}	45,0	36,9
Bluephase	20 s	2,0(0.1)^{d}		46,2 (12,1) $^{a, b, c}$	27,2 (13,6)$^{a, b}$	58,8	46,1
Bluephase	40 s	2,5(0.1)^{e}		47,8 (17,9)$^{a, b, c, d}$	28,9 (14,2) $^{a, b}$	60,4	48,9
MiniL.E.D Fast mode	10 s	1,2(.0.1)^{a}	3,6(0.8)^{b}	41,2 (8,8) $^{a, b, c}$	23,8 (10,5) ^{a}	57,7	40,3
MiniL.E.D Fast mode	20 s	1,4(0.2)$^{b, c, a}$		40,3(8,0)$^{a, b}$	28,3(20,0)$^{a, b}$	70,2	47,9
MiniL.E.D Fast mode	40 s	1,6(0.2)$^{b, c}$		40,8(7,4) $^{a, b, c}$	22,3(12,4) ^{a}	54,6	37,7
MiniL.E.D Pulse mode	10 pulses	1,2(0.1)^{a}	3,6(0.8)^{b}	38,6(11,2)$^{a, b}$	24,9(9,8) $^{a, b}$	64,5	42,2
MiniL.E.D Pulse mode	20 pulses	1,3(0.1)$^{a, b}$		38,0(13,6)^{a}	26,9(14,4)$^{a, b}$	70,7	45,5
MiniL.E.D Pulse mode	40 pulses	1,6(0.1)$^{b, c}$		45,1(12,4)$^{a, b, c}$	31,3(11,6)$^{a, b}$	69,4	53,0
MiniL.E.D Ramping mode	20 s	1,3(0.1)$^{b, c, a}$	7,5(0.3)^{c}	41,9(10,6)$^{a, b, c}$	30,1(14,5)$^{a, b}$	71,8	51,0

- % of Bottom hardness calculated using the bottom and top surface values of the corresponding regimes.

- % of Bottom hardness calculated by dividing the bottom surface HV of each regime by the top surface HV of Astralis 10 40s which is 59.

Table 7.3: Modulus of Elasticity (E) values of the different regimes of the curing units. Homogenous subsets within a Light curing unit are represented by similar superscripts. The standard deviations are represented within the parentheses.

Regimes	Time	Modulus of Elasticity(E) [GPa]	
		Top	Bottom
Astralis 10	10 s	10,1 (1,5) [d]	6,7 (1,7) [a, b, c]
Astralis 10	20 s	9,3 (2,0) [d, c]	7,0 (1,9) [a, b, c]
Astralis 10	40 s	9,9 (2,6) [d]	7,3 (1,9) [b, c]
Bluephase	10 s	7,8 (1,1) [a, b]	5,8 (1,6) [a]
Bluephase	20 s	8,3 (1,6) [a, b, c]	7,2 (2,0) [a, b, c]
Bluephase	40 s	9,0 (2,2) [a, b, c]	7,2 (2,0) [a, b, c]
MiniL.E.D Fast mode	10 s	7,4 (1,5) [a]	5,8 (1,6) [a]
MiniL.E.D Fast mode	20 s	7,4(0,8)[a]	6,7(1,5)[a, b, c]
MiniL.E.D Fast mode	40 s	8,1(1,0)[a, b, c]	6,0(1,7)[a, b]
MiniL.E.D Pulse mode	10 pulses	7,4(1,3)[a]	6,2(1,4)[a, b, c]
MiniL.E.D Pulse mode	20 pulses	8,3(1,9)[a, b, c]	6,6(2,3)[a, b, c]
MiniL.E.D Pulse mode	40 pulses	8,6(1,4)[a, b, c]	7,5(1,9)[c]
MiniL.E.D Ramping mode	20 s	8,1(1,1)[a, b, c]	7,2(1,9)[a, b, c]

Table 7.4 shows the correlation among polymerisation shrinkage stress, gel point, modulus of elasticity (E) and the hardness values (HV).

	Stress	**Gel point**	**E**	**HV**
Stress	1	-0,5(**)	0,1(*)	0,2(*)
Gel point	-0,5(**)	1	-0,1	-0,1
E	0,1(*)	-0,1	1	0,8(**)
HV	0,2(*)	-0,1	0,8(**)	1

(*) represents correlation at a significance level of 0,05.

(**) represents correlation at a significance level of 0,01.

***Figure 7.1*:** A graphical representation of the polymerization shrinkage stresses after 300 s of all the curing units and regimes used in this experiment. Astralis 10 at 40 s yielded the highest stress. Homogenous groups are indicated by linear markings**.**

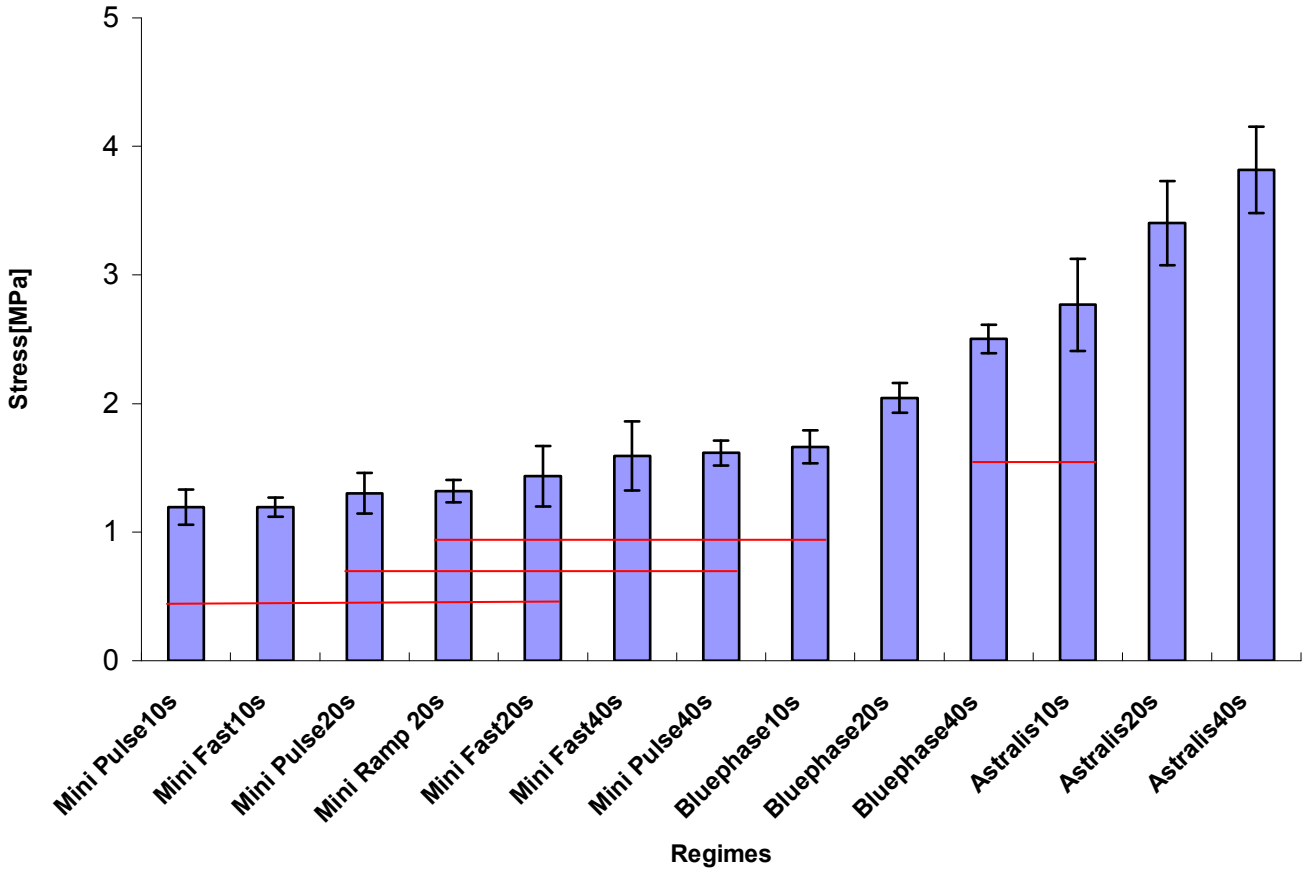


***Figure 7.2*:** Graphical representation of time when the gel point (defined as the force build up above 0.5 N) was reached by the Astralis 10, Bluephase, MiniL.E.D Fast mode, MiniL.E.D Pulse mode and the MiniL.E.D Ramping mode. Statistically significant difference exists between the gel points achieved with Ramping mode when compared to other modes. Homogenous groups are indicated by linear markings.

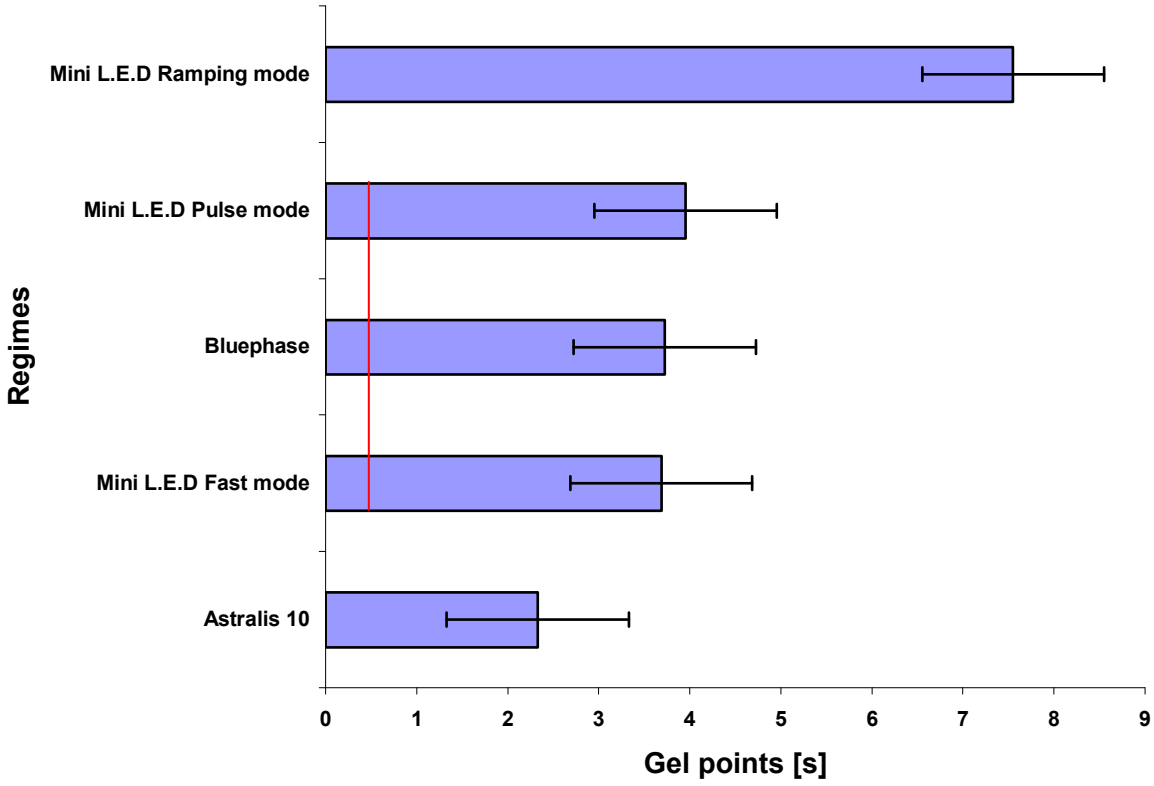


***Figure 7.3*:** Comparison of the curve forms of polymerization shrinkage force achieved during polymerization of Tetric Evo Ceram with Bluephase High Intensity Program at 10 s, 20 s, and 40 s. The progression of curve up to 300s is shown here. When the light curing unit is switched off after 10 or 20 or 40 s a sharp rise in the curve can be appreciated. This is caused by the temperature decrease in the composite after the curing unit is switched off.

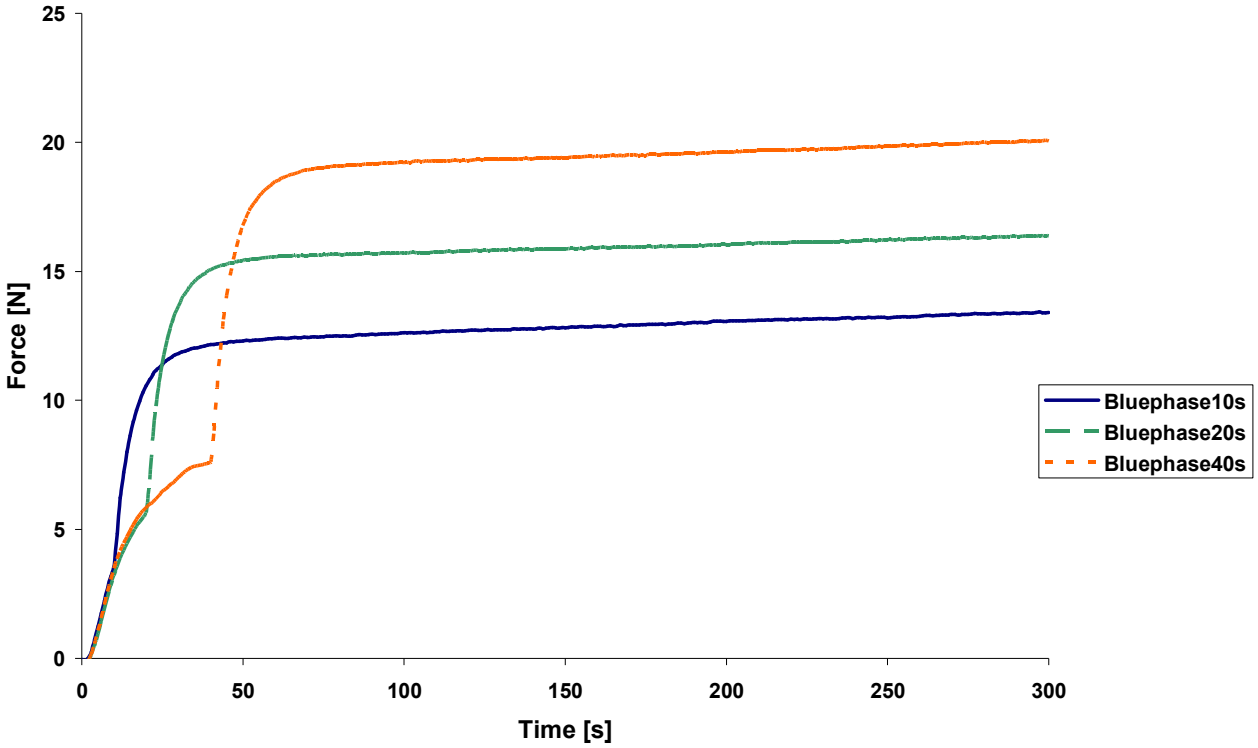
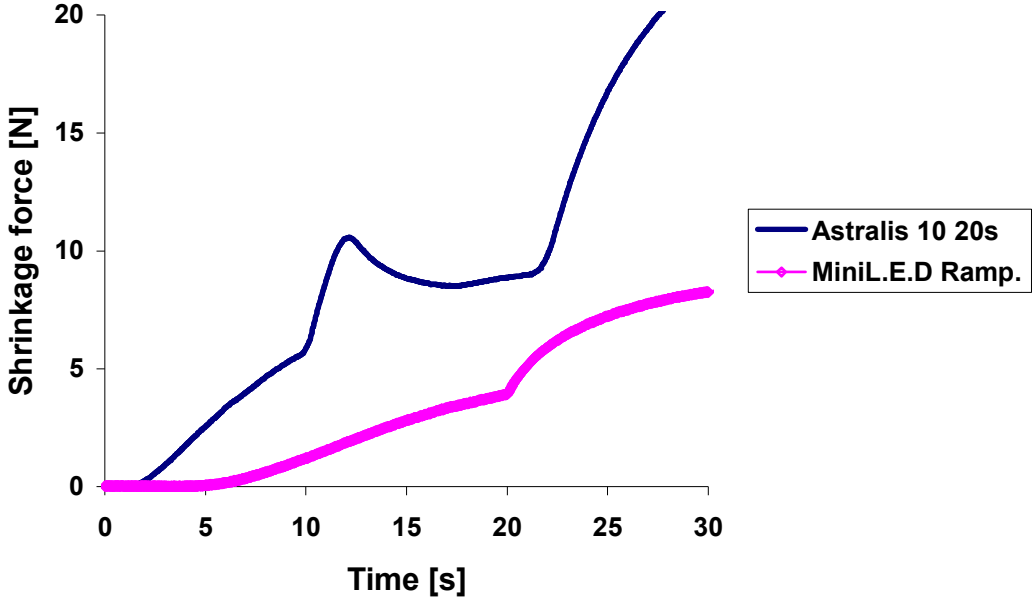


***Figure 7.4*:** Shows the inclination of the curve in Astralis 10 20s and MiniL.E.D Ramping mode. Astralis 10 has a steep inclination whereas the Ramping mode has a gradual inclination. A peak is observed in the curve of Astralis 10 just after 10 s cure. This observed peak indicates the switching on of the light after 10 s irradiation as the timer of the device is set only for 10 s at the HIP by the manufacturer.



Discussion: The force measured by the stress-strain analyser can be visualised in the form of a curve. Figure 7.3 as shown above illustrates the different curves for the Bluephase light curing unit. Details of the curve are important to understand the stress, gel point and the polymerization kinetics. The curve form depends on the type of the material, exposure times, light intensity, distance of the light source and the C-factor. When the light curing unit is switched off after a 10 s exposure there is a steep increase in the curve due to temperature change. Thus, for a 40 s exposure time, switching off the light at every 10 s and switching it on again will immediately produce the same effect and therefore, the dip and sharp rise in the curves are noticeable. During this time, the composite cool down and contracts more. The shape of the curve is the same for the initial few seconds after which the inclination of curve depends on the exposure time and total irradiance.

Figure 7.4 shows the inclination of the slope of the curve for Astralis 10 20s and Ramping mode 20s. This figure is an explanation of the influence of the total irradiance on the gel point and on to the kinetics of the reaction. The reaction kinetics is proportional to the reacting double bonds, the light intensity and the number of initiator molecules. For Astralis 10 20s, the inclination is sharp and is quickly rising compared to the Ramping mode of the MiniL.E.D which increases slowly. Since the light intensity increases only gradually in the Ramping mode, the gel point is prolonged and thereby results in less final stress in comparison with Astralis 10 20s.

When the gel points of Astralis 10 (~2 s) and LED (~3 to 4 s) are compared, the delay in the gel point of the LED is according to the theory. There is associated reduced stress produced by the LED in comparison to Astralis 10. The Pulse mode 20s and Ramping mode 20s of MiniL.E.D are compared because they both are considered to be soft-start programs; they have the

same final intensity and light dose. The gel point of the Ramping mode is twice that of the Pulse mode. If the gel point is proportional to the flow factor, then the Ramping mode alone must have yielded the lowest stress. This is not so, both the Fast mode and the Pulse mode at 20s have yielded similar stresses as that of the Ramping mode. In one of the studies by Koran et al. (Koran and Kurschner, 1998) it was inferred that the ramp curing affected neither the shrinkage nor the mechanical property such as hardness of the composites when the total irradiation dose is comparable to a fast cure or continuous cure protocol so that an adequate degree of conversion is achieved. They also concluded that above a total irradiation dose of 17,000mWs/cm², the surface hardness values remain constant and will be increased no further. The system set-up with a C-Factor of 0.33 allows sufficient flow of the material. The literature speaks about the importance of flow in the relaxation of contraction stresses (Davidson and De Gee, 1984) but in this experiment flow does not seem to be a major factor. The filler component of Tetric Evo Ceram contains pre polymers which may be responsible for the reduction in flow capabilities. Gel point alone is not enough as an explanation to the production of low stresses. What is more important is the inclination of the curve.

The shrinkage stress is less in the soft start mode (Pulse and the Ramping mode) of MiniL.E.D when compared to the High Intensity Program of Astralis 10, but is not significantly lower when compared with the Fast mode of MiniL.E.D itself. It is probable that the effects of soft start depends on the type of the device used i.e. LED or QTH and the light intensity. The effect of soft-start curing depends on the material itself, with the most effective response from hybrid resin-based composites (Ernst *et al,* 2000, Ernst *et al,* 2003). Yap and colleagues reported that though soft-start polymerization

reduced stresses, the reduction of polymerization shrinkage was not of statistical significance and did not affect the effectiveness of cure of the composite Z100 (Yap *et al,* 2001) Ernst et al. state that composites can be cured with soft–start as it does not affect any of the material properties negatively (Ernst *et al,* 2004c). Studies exist, demonstrating the positive influence of the soft-start polymerization approach (Ernst *et al,* 2000, Ernst *et al,* 2003, Feilzer *et al*, 1995), while some newer studies deny this effect (Sahafi *et al*, 2001, Hofmann *et al*, 2003). The positive aspect of soft–start was not accepted by some authors because it is considered that the bonding agents are more important rather than the soft-start procedure itself. From these references, it is apparent that soft start curing has been widely explored for improving the marginal integrity of the composites which in turn is influenced by the polymerization shrinkage stress.

When halogen lamp curing is compared with the LED then the lower stresses of the MiniL.E.D can be due to the reduced number of double bond conversion chemically and not due to stress relaxation by flow (Lu *et al,* 2004a) The stress is highest for Astralis 10. Short gel point and steep inclination of the curve are conclusive of building up of high stresses. It is also important to know that a device like Astralis 10 can produce higher hardness values. Astralis 10 at 40 s exposure produced the highest hardness. It was concluded that halogen curing units can produce higher hardness value of the composites than the L E D (Dunn and Bush, 2002).

It was noted that the curing time did not have any statistically significant influence on the surface micro hardness values within the same curing unit for different curing times. When Astralis 10 and the LED at 10 s, 20 s and 40 s are compared among themselves, the surface hardness values are very

similar within one curing unit for different curing times. This is not as expected because with higher exposure time, the surface properties have to be improved. The surface hardness values measured in this experiment were immediate hardness values and are not the values after 24 h storage in distilled water. Storage in water for longer periods has proved to increase the hardness values of the composite (Ilie, 2004). The results suggest that 10 s light curing is sufficient to achieve comparable hardness values as 20 s and 40 s polymerization. The importance of curing times longer than 10 s probably lies in the improved curing depth with longer curing times (Ilie, 2004) When the composite is irradiated, the camphoroquinone initiators absorb photons and are used up and after some time only the deeper layers are left with the initiators. Since the number of initiators to absorb light decreases in the superficial layers, it is expected that more photons will be available in the bottom layers causing formation of additional radicals. This theory is not reflected in the bottom hardness values because the photons of visible light do not penetrate the composite without losses, photons are lost while breaking the bonds of the initiator and a percentage of them are scattered by the filler particles. Photons decay quickly with penetration depth and their amount will be insufficient to generate sufficient radicals. This theoretically leads to the formation of only short polymer chains and in turn low mechanical property (Šušterčič *et al,* 1997). When hardness profiles are recorded, the hardness decreases with depth (Ilie, 2004).

The literature gives the percentage of bottom/top surface hardness value to be 80% for a properly cured composite stored for 24 h (Pilo and Cardash, 1992), (Ernst *et al*,2004b) and not for the immediate hardness. None of the samples in this experiment attained 80% hardness cut-off value at the depth of 2mm since post curing has not occurred. Post curing is most likely to

occur within 1 h after irradiation and tends to slow down during the 24 h period (Pilo and Cardash, 1992). Since the top surface values of different regimes are not similar this cut off value has its disadvantages while comparing the surface hardness ratios (Dunn and Bush, 2002).

There are two options to determine the percentage of hardness at the bottom.

[a] Is to find the bottom/top hardness percentage with the values of the corresponding regime.

[b] Is to find the bottom/top hardness percentage with a reference value (the highest top surface HV attained). Astralis 10 was never intended by the manufacturer to be used for 40 s in the HIP for clinical use, but in our experiment we used it because of its highest intensity with broad spectrum and to achieve the highest conversion. The top surface HV obtained with Astralis 10 at 40 s exposure time stands as a reference value for the sake of delineation of improperly cured material. While looking into the data of hardness values for the different LCU and regimes at the bottom surface, it is observed that they are also similar. This is actually not expected because higher intensity light must yield more hardness (Dunn and Bush, 2002). This may be due to the incomplete polymerization reaction soon after the material is being cured. Post-curing thus will play a vital role to increase the surface hardness. When option [a] is considered then the highest HV for the bottom is obtained for MiniL.E.D Ramping mode 20s. When option [b] is considered the highest HV is reached by Astralis 10 40s. It is difficult to announce any of this value to be the optimum HV because of the non-standardisation existing in the research field. The value above which the composite is considered to be sufficiently cured has to be ascertained in the future studies as a step towards standardisation. The attainable % of bottom HV for MiniL.E.D is 60-70% whereas for Bluephase and Astralis 10 it is 50-

60% only. The 24 h measurements were not done in this experiment. It is likely that the high intensity lamps attain a slow but a better gain in HV due to post curing than the low intensity lamps. One suggested way to standardise is to use a deeper location to determine the hardness value rather than the surface hardness, for example, HV at 2mm depth as a reference and another threshold like 95% of the top surface HV for the bottom. It was also proposed that bottom layer hardness can be a more useful measure of the degree of polymerization than the top surface hardness (Šušterčič *et al,* 1997).

Though the mechanical properties within different curing regimes are similar, the shrinkage stress values differ significantly. This implies that there can be a better relationship between exposure time and contraction stress than for the exposure time and surface hardness values. In other words, the exposure times influence the shrinkage force and stress values more than the surface hardness values. This makes it important for the dentist while restoring the teeth to minimize stresses at the teeth-restoration interface. In an interesting work by Bouschlicher et al.(Bouschlicher *et al,* 2000) the importance of exposure time is appreciated in determining the polymerization shrinkage force. It was also observed that the hardness values at different exposure times for the two LEDs used in this study showed no statistical significant differences, but there were differences in the stress values. For example, the stress of the Pulse mode at 10 s for the MiniL.E.D was statistically significantly lower than that of Bluephase at 10 s. The reason may be the low heat production of the MiniL.E.D but this was not evaluated in this study. So, with minimum exposure, minimal shrinkage force as well as good surface hardness values can be achieved. Accordingly,

one line of thought will be that with a good light intensity one can establish less shrinkage forces in 10 s along with good hardness than to unnecessarily increase the exposure time and also increase the stress with no positive effect on the hardness values. Hansen and Asmussen in their work have stated that surface hardness does not help to qualify the curing units' performance because the depth of cure is important rather than just surface hardness (Hansen and Asmussen, 1993) Therefore, surface hardness alone cannot be a reliable indicator of the quality of curing.

It is statistically evident that the curing contraction stress of LED Bluephase (prototype) at 40 s is similar to the halogen Astralis 10 at 10 s. Both light intensity and exposure time are important factors in determining the curing properties of the composites (Althoff, 2000). Astralis 10 is a high intensity curing unit. A slightly lower intensity LED curing unit such as Bluephase can result in comparable results regarding the polymerization shrinkage stress and micro hardness when the exposure time is increased. It is evident from few research works that though the source is of low intensity, it is possible to produce better degrees of conversion if the irradiation time is increased. This suggests that a lower intensity can be compensated by increasing the curing time (Discacciati *et al*, 2004).
Modulus of elasticity and hardness are indirect indicators of the quality of polymerization. Asmussen (Asmussen, 1982) showed that, for a given resin composite, mechanical properties are a good indication of the degree of conversion. Based on such a theory, it was observed that the low stress producing Pulse mode at 10 s also produces low values of elastic modulus which means less stiffness of the composite. Heavy cross linking and entanglements of the polymer network are associated with higher elastic

modulus (Lim *et al*, 2002). High modulus of elasticity is one of the factors generating higher early stresses (Sakaguchi *et al,* 1992). It was also statistically evident from the correlation that stress and the indentation modulus are correlated. So it is essential to select a regime that would mean less stress production and at the same time good material stiffness and hardness. A LCU which can influence the composite intermediately can be utilised so that no compromises are made upon the properties and at the same time no high stresses are produced. Bluephase HIP at 40 s and MiniL.E.D Pulse mode at 40 s can be suitably used to produce such optimal properties. It was reported in one of the studies by Peutzfeldt et al. that the conventional method of curing for 20 to 40 s with the intermediate power density LCU can produce favourably cured material (Peutzfeldt and Asmussen, 2004)

Conclusion: Curing time plays an important role in assessing stresses produced during the polymerization shrinkage of dental composites. High intensity light curing units produce not just high hardness values but also high shrinkage, making it important to balance both the effects by selecting the correct curing time. With a LED like MiniL.E.D significant differences in the behaviour of composite by different curing regimes can not be observed. Soft-start regimes have no paramount benefit in a LED regarding stresses in the clinical situation. The soft start polymerization doesn't provide any added advantage based on the stress and mechanical properties analysed from this experiment for use in the clinical situation. Standardisation is required for immediate and 24 h hardness values at the bottom surface of the composite.

(ii) Comparison of the behavioural properties of a nano-optimised composite (Tetric Evo Ceram) and a micro-hybrid composite (Tetric Ceram).

Introduction: Tetric Ceram is a micro-hybrid composite and has been regarded as a composite with wholesome property. The manufacturer has improvised this composite by modifying the filler particles with prepolymers and nanofillers to create Tetric Evo Ceram, an evolutionary product of Tetric Ceram.

Objective: Our aim in this study was to perform the shrinkage stress measurement tests with similar light curing units on both these composites and to also measure the mechanical properties for comparative purposes.

Results: The results are compared in the Tables 7(ii) 1 and 2

Table7(ii)1: Stress values of Tetric Evo Ceram and Tetric Ceram

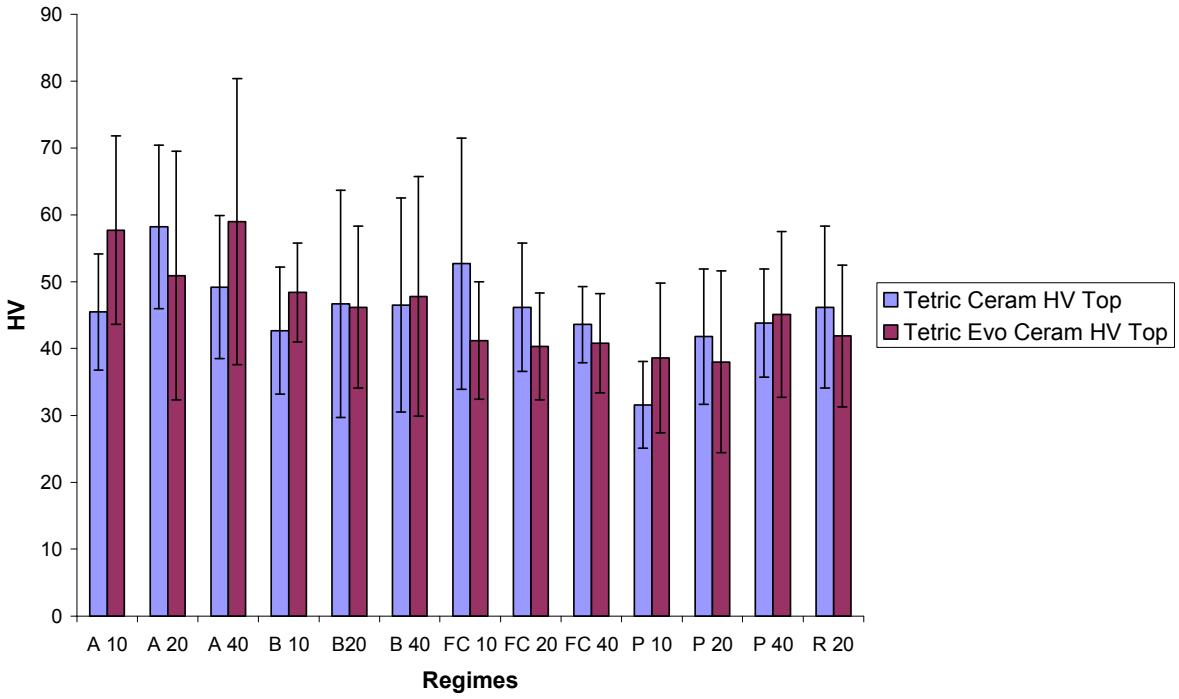
Regimes	Tetric Evo Ceram Stress [MPa]	Tetric Ceram Stress [MPa]
Astralis 10 10s	2,7 (0,3) ^{e}	2,9 (0,5)^{f,g}
Astralis 10 20s	3,4 (0,3) ^{f}	3,5 (0,3)^{h}
Astralis 10 40s	3,8 (0,3) ^{g}	3,8 (0,3)^{h}
Bluephase 10s	1,6(0,1)^{c}	2,5 (0,2)^{d,e,f}
Bluephase 20s	2,0(0,1)^{d}	2,6 (0,2)^{e,f,g}
Bluephase 40s	2,5(0,1)^{e}	3,0 (0,2)^{g}
MiniL.E.D Fast mode 10s	1,2(,0,1)^{a}	1,4 (0,1)^{a}
MiniL.E.D Fast mode 20s	1,4(0,2)$^{b, c, a}$	2,1 (0,1)^{b,c}
MiniL.E.D Fast mode 40s	1,6(0,2)$^{b, c}$	2,4 (0,1)^{c,d,e}
MiniL.E.D Pulse mode 10s	1,2(0,1)^{a}	1,7 (0,1)^{a,b}
MiniL.E.D Pulse mode 20s	1,3(0,1)$^{a, b}$	2,2 (0,1)^{c,d}
MiniL.E.D Pulse mode 40s	1,6(0,1)$^{b, c}$	2,3 (0,1)^{c,d,e}
MiniL.E.D Ramping mode 20s	1,3(0,1)$^{b, c, a}$	2,0 (0,1)^{b,c}

Table 7 (ii) 2: Modulus of elasticity values of Tetric Evo Ceram and Tetric Ceram

Regimes (20 s)	Tetric Evo Ceram	Tetric ceram
Astralis 10	9,7 (2,0)	10,4 (1,5)
Bluephase	8,3(1,6)	8,4(1,5)
Fast mode	7,4 (0,8)	8,3 (0,9)
Pulse mode	8,5 (1,8)	7,3 (0,6)
Ramping mode	8,2 (1,1)	7,5 (1,7)

Also, here with the elastic modulus values, Tetric Evo Ceram is doing better than Tetric Ceram when light modulation is done.

Figure 7 (ii) 1: Hardness values compared between Tetric Evo Ceram and Tetric Ceram.



When the hardness values of Tetric Evo Ceram and Tetric Ceram are compared, they almost come under the same range of values.

Discussion: Based on the statistics there are no significant differences between Tetric Evo Ceram and Tetric Ceram for all curing units and curing times except the Pulse and Ramping modes. This implies that high intensity lamps like Astralis 10 and Bluephase do not bring about much change in the composites with prepolymers whereas a low intensity lamp can produce difference in the stress levels. Composite with prepolymers such as Tetric Evo Ceram are reactive to low intensity lamps than to high intensity. The contraction stress of a nano-filled composite is significantly low than when compared to a micro-hybrid composite when light modulation is done. This would mean that when a composite with prepolymers is used in clinical use with an intention to reduce the contraction stress then it should be accompanied by light modulation otherwise the positive effect is lost.

Chapter 8

Filtek Supreme- a Nanocomposite- Influence of distance on the curing properties

Introduction: Filtek supreme is a nanocomposite with the silica particles arranged in clusters, consisting of isolated nanofillers. Nanocomposite is advancement in the manufacturing of the dental composites.

Objective: The aim of the study was to determine the influence of varying distances on the curing properties of Filtek Supreme.

Material and methods: Filtek Supreme with LOT NO: 3BE and A3 shade was used. The composite was cured at distances of 0mm, 1mm, 2mm and 4mm. An exposure time of 20 s was set. The curing units were Astralis 10, Bluephase and MiniL.E.D [Fast mode, Pulse mode and Ramping mode]. For Filtek Supreme, the mechanical properties were measured immediately after curing and also after 24 hours.

Results: The following are the results of the study.

Table 8.1: Shrinkage force, polymerization shrinkage stress and gel point for the distances of 0mm, 1mm, 2mm and 4mm with the LCU Astralis 10, Bluephase and MiniL.E.D for an exposure time of 20 s.

Light curing units	Exposure time	Distances [mm]	Force [N]	Stress [Mpa]	Gel Point [s]
Astralis 10	20 s	0	31,2(4,6)^{i}	3,9(0,6) ^{k}	2,7 (0,3) ^{a,b}
	20 s	1	29,1(4,4) ^{h,i}	3,6(0,5) ^{j,k}	2,7(0,2)^{a,b}
	20 s	2	27,4(1,4) ^{g,h,i}	3,4(0,2) ^{i,j,k}	3,0(0,3)^{a,b}
	20 s	4	19,8(2,0) ^{a,b,c,d,e}	2,5(0,3) ^{a,b,c,d,e,f,g}	4,3(0,1)^{d,e}
Bluephase	20 s	0	24,6(0,9) ^{e,f,g,h}	3,1(0,1) ^{g,h,i,j}	2,5(0,3)^{a}
	20 s	1	24,2(1,0) ^{e,f,g,h}	3,0(0,1) ^{g,h,i,j}	3,0(0,2)^{a,b,c}
	20 s	2	23,3(1,6)d, ^{e,f,g,h}	2,9(0,2) ^{e,f,g,h,i,j}	3,1(0,1)^{a,b,c}
	20 s	4	18,0(2,4) ^{a,b,c,d}	2,2(0,3) ^{a,b,c,d,e,f}	4,0(0,4)c,d,e
MiniL.E.D Fast mode	20 s	0	26,2(1,2) ^{f,g,h,i}	3,2(0,1) ^{h,i,j,k}	2,6(0,1)^{a,b}
	20 s	1	23,2(3,0)d, ^{e,f,g,h}	2,8(0,4) ^{d,e,f,g,h,i}	3,1(0,4)^{a,b,c}
	20 s	2	17,7(2,6)^{a,b,c,d}	2,2(0,3) ^{a,b,c,d,e}	3,5(0,7)^{a,b,c,d}
	20 s	4	15,0(1,8)^{a,b}	1,8(0,2) ^{a,b}	4,9(0,5)^{e,f}
MiniL.E.D Pulse mode	20 pulses	0	24,1(4,0) ^{e,f,g,h}	3,0(0,5) ^{f,g,h,i,j}	2,9(0,4)^{a,b}
	20 pulses	1	21,5(2,5) ^{c,d,e,f,g}	2,6(0,3) ^{c,d,e,f,g,h}	3,6(0,4)^{b,c,d}
	20 pulses	2	20,8(2,8) ^{b,c,d,e,f}	2,6(0,3) ^{b,c,d,e,f,g,h}	3,6(0,8)^{b,c,d}
	20 pulses	4	15,6(1,3) ^{a,b,c}	1,9(0,2) ^{a,b,c}	5,7(0,5)^{f,g}
MiniL.E.D Ramping mode	20 s	0	21,1(2,6) ^{c,d,e,f}	2,6(0,3) ^{c,d,e,f,g,h}	6,1(0,2)^{g,h}
	20 s	1	20,1(3,2) ^{b,c,d,e}	2,5(0,4) ^{b,c,d,e,f,g,h}	6,8(0,4)^{h,i}
	20 s	2	17,0(1,9) ^{a,b,c}	2,1(0,2) ^{a,b,c,d}	7,5(0,3)^{i}
	20 s	4	14,0(2,6) ^{a}	1,7(0,3) ^{a}	8,8(0,8)^{j}

The highest stress values were obtained by Astralis 10 at 0 mm distance whereas the lowest was achieved by the Ramping mode at a distance of 4 mm.It is significant to note that though the stress values within the LCU MiniL.E.D are comparable, the gel point of the Ramping mode is very high when compared to Fast mode or the Pulse mode. Here, shrinkage stress relaxation prior to the vitrification did not provide significant benefit towards the reduction of the overall shrinkage stress due to much longer stress relaxation time required as compared to the clinically practical time scale. The benefit of using lower initial light intensity to relieve shrinkage stress prior to gelation period is very limited (Lu *et al*, 2004a).

Table 8.2: The Hardness Value at the top and bottom along with bottom to top surface hardness ratio at 0 and 24 h after curing.

Light curing units	Distance s [mm]	HV Top-0 h	HV Bottom-0 h	% B/ T 0 h	HV Top- 24 h	HV Bottom-24 h	% B/ T 24 h
Astralis 10 (20 s)	0	89,8 (10,7)^{h}	78,8(9,8)^{h}	87,8	90,7(7,4)^{g}	81,4(12,7)g	89,7
	1	93,2 (5,5)^{h}	76,6(7,4)^{h}	82,2	91,3(7,9)^{g}	79,3(9,2)g	86,9
	2	87,9(0,6)^{h}	72,2(6,8)^{g,h}	82,1	84,1(6,4)^{f,g}	76,0(8,7)f,g	90,4
	4	76,5(7,5)^{g}	62,8(11,5)^{e,f}	82,1	80,8(11,7)^{e,f}	68,3(11,3)d,e,f	84,5
Bluephase (20 s)	0	74,2(6,0)^{f,g}	73,4(8,9)^{g,h}	98,9	75,6(7,2)^{b,c,d,e}	80,5(11,1)g	106,5
	1	70,8(6,2)^{d,e,f,g}	66,8(5,8)^{f,g}	94,4	69,6(13,2)^{a,b,c,d}	68,9(7,0)d,e,f	99,0
	2	74,2(8,1)^{g}	60,9(7,2)^{d,e,f}	82,1	77,9(9,2)^{d,e,f}	63,8(12,7)d,e	81,9
	4	66,8(9,9)^{b,c,d,e}	54,1(6,7)^{b,c,d}	81,0	72,1(6,8)^{a,b,c,d}	59,1(7,0)d,c,d	82,0
MiniL.E.D Fast mode (20 s)	0	59,0(5,0)^{a}	59,8(10,5)^{c,d,e,f}	101,4	73,2(6,8)^{a,b,c,d,e}	69,1(9,3)d,e,f	94,4
	1	64,6(5,9)^{a,b,c,d}	62,8(9,1)^{e,f}	97,2	68,4(10,6)^{a,b,c}	62,8(10,6)c,d	91,8
	2	65,9(5,1)^{a,b,c,d,e}	52,2(7,1)^{b,c}	79,2	65,8(9,0)^{d}	63,1(14,7)c,d	95,9
	4	64,0(7,4)^{a,b,c,d}	47,8(5,6)^{a,b}	74,7	70,9(11,7)^{a,b,c,d}	50,1(9,6)a,b	70,7
MiniL.E.D Pulse mode (20 pulses)	0	68,9(9,5)^{c,d,e,f}	66,8(14,7)^{f,g}	97,0	71,9(11,0)^{a,b,c,d}	73,1(13,7)e,f,g	101,7
	1	67,4(7,7)^{b,c,d,e,f,g}	61,7(8,4)^{d,e,f}	91,5	72,7(7,7)^{a,b,c,d,e}	66,7(9,3)d,e,f	91,7
	2	69,4(9,5)^{c,d,e,f,g}	58,9(9,5)^{c,d,e,f}	84,9	72,0(5,4)^{a,b,c,d}	63,3(10,6)c,d	87,9
	4	63,7(7,7) ^{a,b,c,d}	51,2(10,1)^{b,c}	80,4	67,4(9,8)^{a,b}	54,3(9,7)b,c	80,6
MiniL.E.D Ramping mode (20 s)	0	60,5(4,8) ^{a,b}	55,4(11,1)^{b,c,d,e}	91,6	71,2(8,1)^{a,b,c,d}	65,0(9,2)d,e	91,3
	1	72,3(8,0) ^{e,f,g}	58,5(9,9)^{c,d,e,f}	80,9	77,7(6,9)^{d,e,f}	62,2(6,1)c,d	80,1
	2	70,6(5,2) ^{d,e,f,g}	57,9(7,6)^{c,d,e}	82,0	76,4(8,8)^{c,d,e,f}	60,4(5,9)c,d	79,1
	4	62,6(6,3) ^{a,b,c}	39,8(7,6)^{a}	63,6	68,5(8,4)^{a,b,c}	44,0(3,1)a	64,2

Table 8.3: The Modulus of elasticity at the top and bottom for 0h and 24 h after curing.

Light curing units	Distances [mm]	Modulus of elasticity –Top-0 h	Modulus of elasticity-Top- 24 h
Astralis 10 (20 s)	0	12,7 (2,0) ^{g,h}	13,7 (1,2) ^{d,e,f}
	1	13,1 (1,0) ^{h}	14,3 (1,3) ^{f}
	2	12,2 (1,3) ^{e,f,g,h}	12,6 (1,9) ^{b,c,d,e}
	4	12,3 (1,2) ^{f,g,h}	13,8 (1,6) ^{e,f}
Bluephase (20 s)	0	11,0 (1,1) ^{b,c,d,e}	12,8 (1,6) ^{c,d,e,f}
	1	11,1 (1,6) ^{c,d,e}	11,8 (2,3) ^{a,b,c}
	2	11,1 (1,3) ^{c,d,e,f}	12,5 (1,8) ^{b,c,d,e}
	4	11,0 (1,2) ^{b,c,d,e}	12,1 (1,6) ^{a,b,c}
MiniL.E.D Fast mode (20 s)	0	9,5 (0,8) ^{a}	11,5 (1,7) ^{a,b,c}
	1	10,6 (1,1) ^{a,b,c,d}	12,2 (2,1) ^{a,b,c,d}
	2	10,8 (1,1) ^{b,c,d}	12,0 (1,5) ^{a,b,c}
	4	10,3 (1,1) ^{a,b,c}	11,9 (2,1) ^{a,b,c}
MiniL.E.D Pulse mode (20 pulses)	0	10,8 (0,9) ^{b,c,d}	12,2 (1,6) ^{a,b,c,d}
	1	10,8 (1,3) ^{b,c,d}	12,2 (1,7) ^{a,b,c,d}
	2	9,8 (1,1) ^{a,b}	11,0 (1,5) ^{a,b}
	4	10,8(1,1) ^{b,c,d}	10,8 (1,2) ^{a}
MiniL.E.D Ramping mode (20 s)	0	10,3 (0,7) ^{a,b,c}	12,8 (1,4) ^{c,d,e,f}
	1	11,7 (0,7) ^{d,e,f,g}	12,6 (1,0) ^{b,c,d,e}
	2	11,2 (1,1) ^{c,d,e,f}	12,9 (1,5) ^{c,d,e,f}
	4	9,8 (1,1) ^{a,b}	10,7 (2,0) ^{a}

Figure 8.1: Shrinkage stress in mega Pascals for the distances of 0mm, 1mm, 2mm and 4mm.

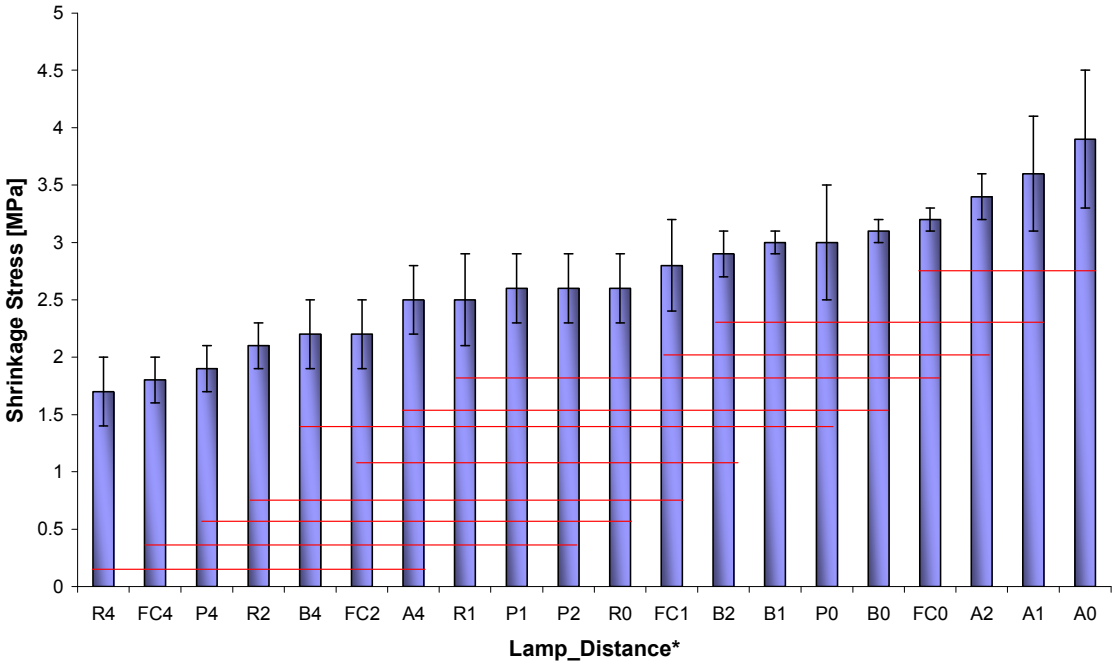
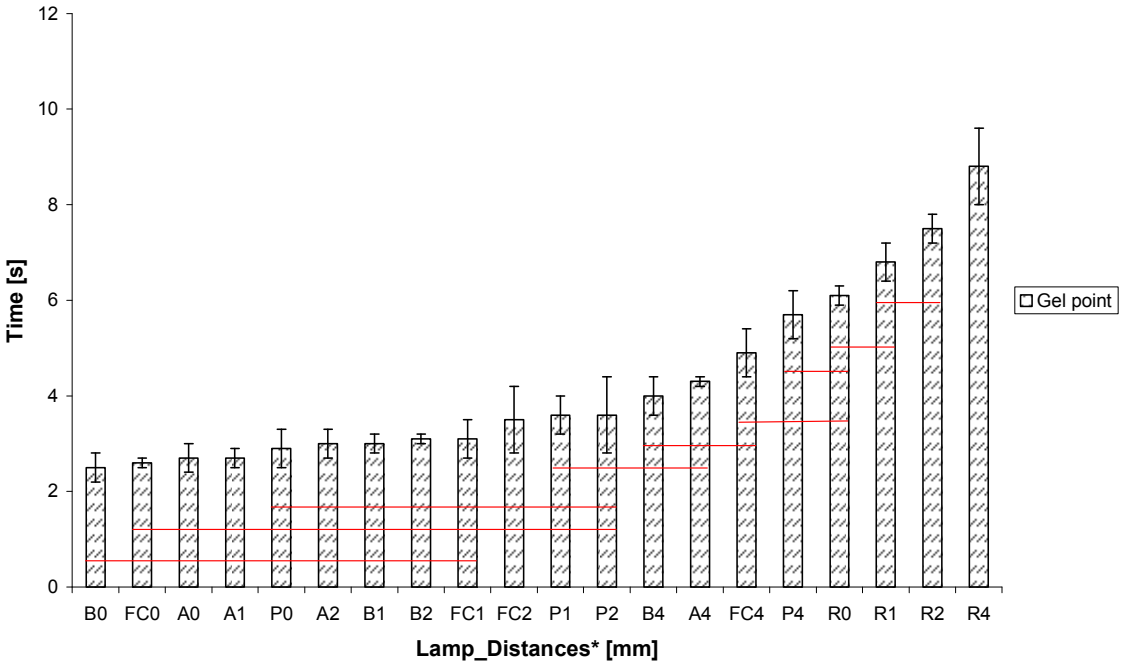


Figure 8.2: Gel points for the distances of 0mm, 1mm, 2mm and 4mm are shown above graphically. Considering the gel point or gel time, the Ramping mode has the longest gel point for all distances of 0, 1, 2 and 4mm.



*-A0, A1, A2, A4= Astralis 0, 1, 2 and 4mm resp.
B0, B1, B2, B4= Bluephase 0, 1, 2 and 4mm resp.
FC0, FC1, FC2, FC4= MiniLED Fast mode 0, 1, 2 and 4mm resp.
P0, P1, P2, P4= MiniLED Pulse mode 0, 1, 2 and 4mm resp.
R0, R1, R2, R4= MiniLED Ramping mode 0, 1, 2 and 4mm resp.

Figure 8.3: Comparison of the hardness values between 0 h and 24 h at the top surface of the polymerized Filtek Supreme composite.

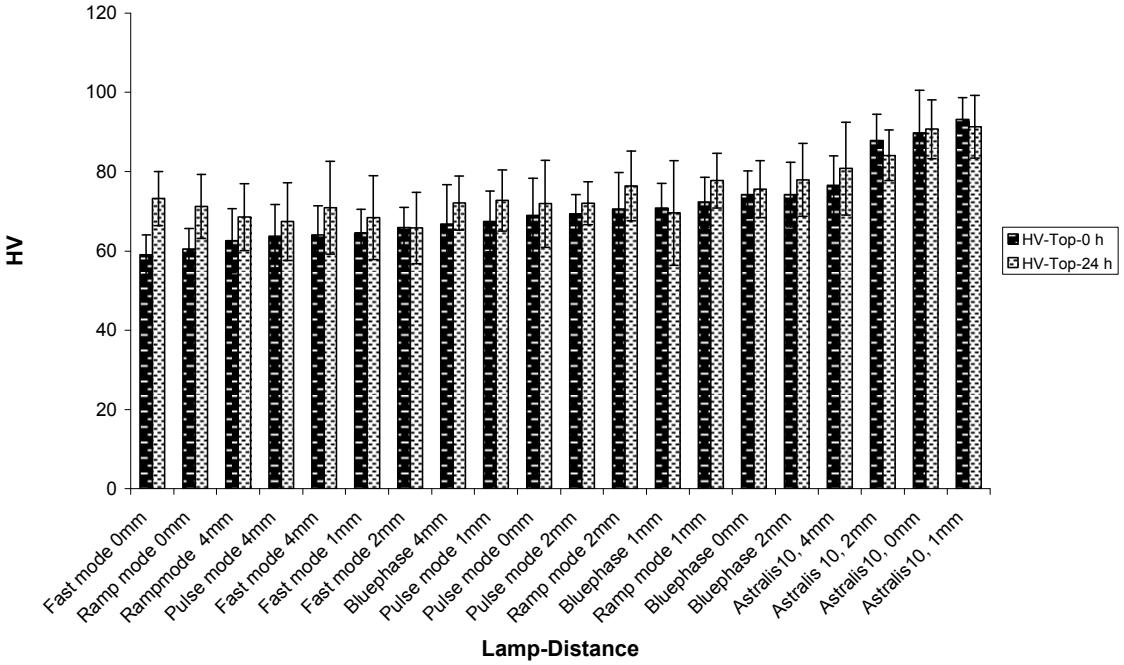
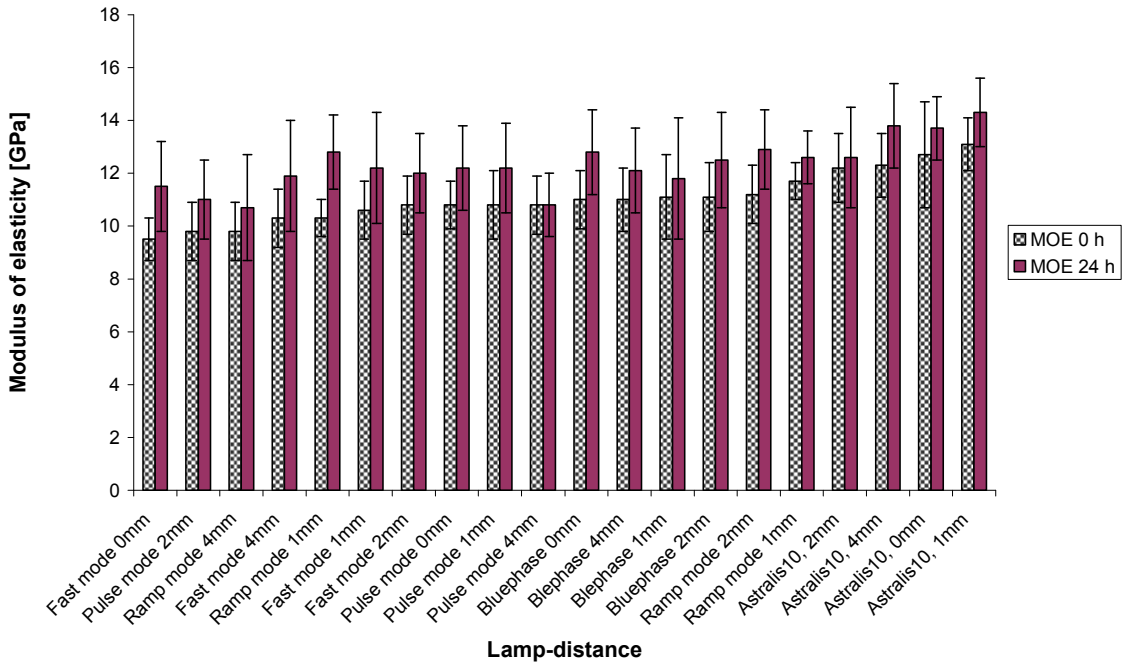


Figure 8.4: Comparison of the modulus of elasticity values for 0h and 24 h for the composite, Filtek Supreme.



Discussion: When the percentage of hardness is calculated for all the distances, we were able to get an overall view of which distances produced adequate hardness and which distances did not. Accordingly, it was noticed that the Ramping and Fast mode at 4mm did not adequately cure the composite. Astralis 10 cured the composite adequately for all distances. Bluephase is good for distances 0 and 1mm but cured borderline at 2 and 4mm. The Pulse mode is good at all distances except 4mm for which it is intermediate.

Now that we know from the hardness data that Astralis 10 produced the best hardness values, we will look into the stress values so that a selection of the best way to cure can be obtained. *Curing the composite with the tip a few millimetres away from the restoration produces less stress without a*

compromise in the hardness up to a distance of 4mm. During the procedure of restoration, the dentist may not have a reference point to keep away the tip exactly at a limit within 4mm. Therefore the safest measure is to use the tip as close as possible but also choose a lamp which produces comparatively less stress. Based on such a point *Ramping mode of the MiniL.E.D will qualify for producing the least stress for a distance of 0mm and also yield a 91% hardness cut-off.* However, these conclusions are limited to the composite, light curing units and exposure times that are used in this experiment and no effort is being made to generalise it universally. From the Hardness Value and Modulus of elasticity values, the highest and lowest values are as follows.

The highest HV and MOE 0 h and 24 h are Astralis 10 at 1mm. The lowest HV and MOE at 0h is Fast mode at 0mm for MiniL.E.D and for 24 h it is Fast mode at 2mm for the same MiniL.E.D. The HV and MOE values do not go hand in hand for the different distances. The response to hardness and rigidity by the composite differs. Since hardness and modulus of elasticity are independent of each other, and as more and more distances of the tip of the light source to the composite are considered, the complexity of the relation between HV and MOE increases. Astralis10 being the powerful lamp remains undisturbed and the HV and MOE values correspond in the order to each other. With three different modes in MiniL.E.D and four different distances in each mode, the values of the regimes of MiniL.E.D are sandwiched between Astralis 10 and Bluephase LCU.

EXTENSION OF THE FILTEK SUPREME STUDY

In an attempt to understand as to what happens when the distance of the composite is increased from the light source, two new distances were chosen. They were 10mm and 20mm.

This small extension study was useful to understand the behaviour of the light curing units.

When the shrinkage curves of all the LCU were compared it was found that at a distance of 10mm, Astralis 10 stood with the maximum contraction stress followed by Fast mode, Bluephase, Pulse mode and the Ramping mode. At 20 mm, it was observed that the shrinkage stress of Astralis 10 has reduced considerably and Bluephase yielded the highest stress followed by Fast mode, Astralis 10, Pulse mode and the Ramping mode. This observation strongly supports the fact that for a high intensity lamp like Astralis 10 with turbo tip, the stress due to shrinkage on the composite is enhanced by heat and temperature increase, which eventually decreases as the distance increases due to dissipation of heat energy.

Also it is noticeable that the sharp dips and rise in the curves as the light is switched on and off are missing. The curve seems to be continuous without any bends. As the distances increase, the pronounced curve effects are decreased. This comparison is shown in Figures 8.5 and 8.6

Figure 8.5: Shrinkage curves for the curing units for a distance of 0mm. Astralis 10 yield the highest contraction force.

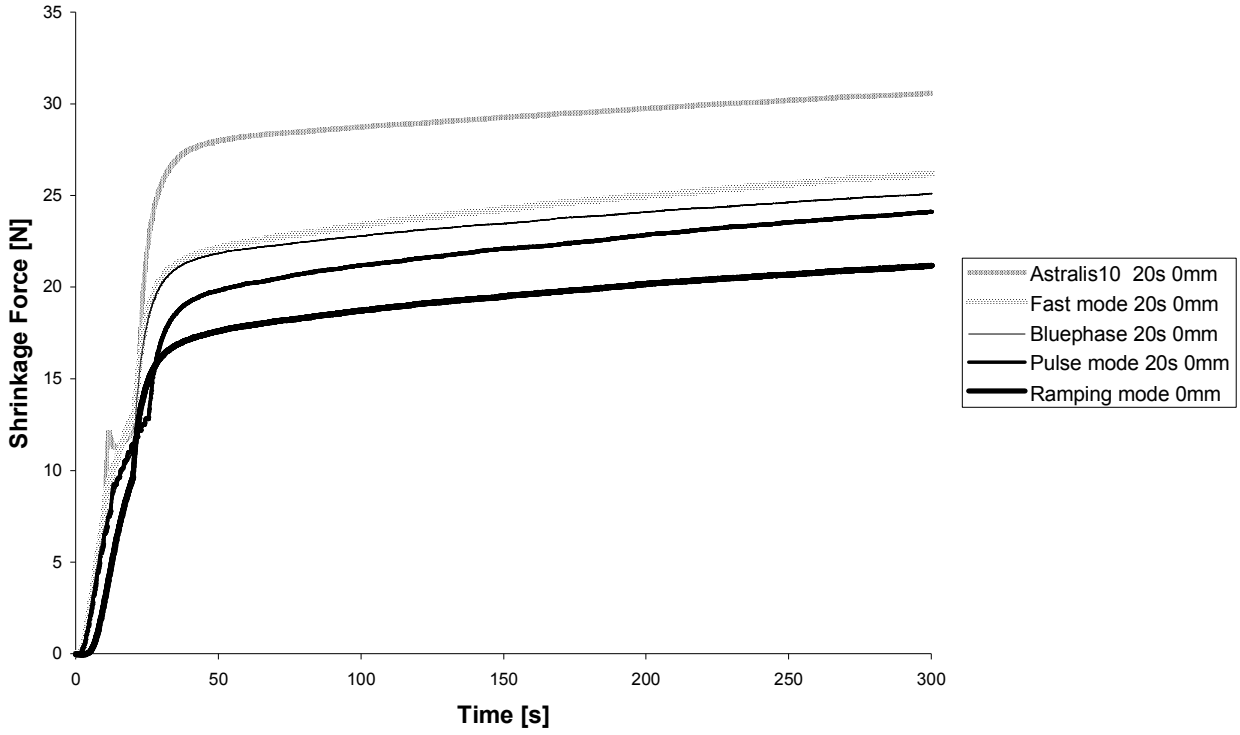


Figure 8.6 : Shrinkage force curves for the light curing units at a distance of 20 mm. When compared to Figure 8.5, the difference at a distance of 20mm is that Bluephase rather than Astralis 10 produced the greatest contraction force implying that heat is dissipated leading to decreased stress production by Astralis 10.

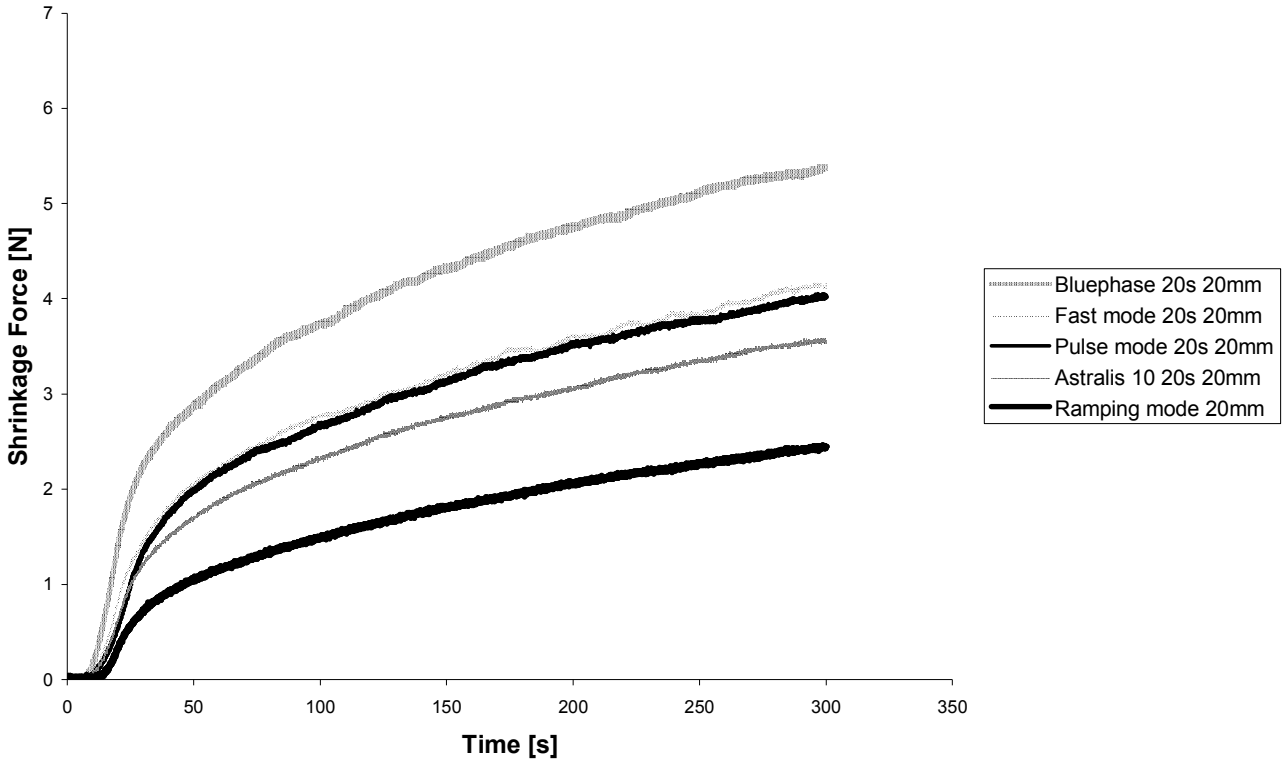


Table 8.4: Hardness values at the top surface for distances 10 and 20 mm. The hardness values at the bottom are not mentioned here because the

composite almost did not cure completely at these distances and were too soft to be placed under the Fischerscope for measurements.

LCU	HV TOP 10mm	HV TOP 20mm
Astralis 10	57,2(10,7)	46,3(9,8)
Bluephase	65,6(7,6)	54,0(12,7)
MiniL.E.D Fast mode	63,8(12,9)	46,3(11,1)
MiniL.E.D Pulse mode	66 0(17,7)	51,5(14,6)
MiniL.E.D Ramping mode	59,1(11,4)	42,9(15,8)

The hardness values achieved by Bluephase are better than the hardness values achieved by Astralis 10 for the distances 10 mm and 20 mm. This again is relevant and corresponds with the stress values as shown in Table 8.5

Table 8.5: Stress values for 10mm and 20 mm.

LCU	***Stress 10mm***	***Stress 20mm***
Astralis 10	1,9 (0,1)	0,4 (0,1)
Bluephase	1,9 (0,06)	0,7 (0,1)
MiniL.E.D Fast mode	1,4 (0,2)	0,5 (0,1)
MiniL.E.D Pulse mode	1,4 (0,2)	0,5 (0,1)
MiniL.E.D Ramping mode	1,2 (0,1)	0,3 (0,03)

Chapter 9

Venus-Color Adaptive Matrix

Introduction: Venus is a micro hybrid composite.

Material and methods: The experiments with Venus were conducted similar to Tetric Ceram as explained in Chapter VI. LOT NO: 010107, A3 shade was used. Eight samples per group were done.

Results: The results are tabulated as follows. Statistical analyses were done using one-way ANOVA, post hoc-Tukey ($p<0.05$) and linear regression.

Table 9.1: Contraction stress, gel point, hardness values (top and bottom) and the modulus of elasticity (top and bottom) for all the 13 regimes. Mechanical property values are the 0h values without post curing.

Regimes	Time]	Stress [MPa]	Gel-point [s]	HV- Top	HV-Bottom	Modulus of elasticity-Top	Modulus of elasticity-Bottom
Astralis10	10s	3,3(0,2)^{g}	2,8(0,2)^{a}	49,6(9,2) ^{b,c,d}	34,6 (11,5)^{a,b}	8,8(1,3) ^{c,d}	8,1 (2,0)^{d,e}
	20s	4,1(0,3)^{h}		56,6(8,2) ^{d}	33,5(10,5)^{a,b}	9,5(1,5) ^{d}	7,9 (2,0)^{c,d,e}
	40s	4,7(0,2)^{i}		57,7(7,6) ^{d}	40,0 (10,4)^{a,b}	9,8(1,0) ^{d}	8,8 (1,7)e
Bluephase	10s	2,6(0,1)^{e}	2,8(0,2)^{a}	47,0(13,3) ^{a,b,c}	34,4 (10,9)^{a,b}	7,9(1,7) ^{b,c}	6,5 (1,7)^{a,b,c,d}
	20s	3,0(0,1)^{f}		50,4(10,5) ^{b,c,d}	33,6 (17,8)^{a,b}	8,1(1,1) ^{b,c}	4,9 (3,4)^{a,e}
	40s	3,3(0,1)^{f,g}		55,2(8,5) ^{d,c}	44,7 (13,5)^{b}	8,6(1,2) ^{c,d}	7,6 (1,9)^{b,c,d,e}
MiniL.E.D Fast mode	10s	2,0(0,2)^{a,b}	3,0(0,6)^{a}	40,1(9,6) ^{a}	25,8 (12,8)^{a}	7,1(1,4) ^{a,b}	5,6 (1,3)^{a,b}
	20s	2,3(0,2)^{c,d,e}		46,1(13,9) ^{a,b,c}	33,5 (11,1)^{a,b}	6,9(0,9) ^{a,b}	5,7 (1,7)^{a,b}
	40s	2,4(0,1)^{c,d,e}		41,9(8,6) ^{a,b}	41,6 (18,6)^{b}	7,1(0,9) ^{a,b}	6,0 (1,8)^{a,b,c}
MiniL.E.D Pulse mode	10 pulses	1,9(0,2)^{a}	3,1(0,6)^{a}	38,9(8,7) ^{a}	36,3 (13,1)^{a,b}	6,3(1,5) ^{a}	5,1 (1,4)^{a}
	20 pulses	2,2(0,2)^{b,c,d}		51,9(11,6) ^{d,c}	45,7 (17,1)^{b,c}	8,1(1,5) ^{b,c}	6,2 (2,5)^{a,b,c}
	40 pulses	2,6(0,2)^{d,e}		46,0(11,1) ^{a,b,c}	59,9 (26,7)^{c}	7,6(1,3) ^{a,b,c}	7,6 (1,2)^{b,c,d,e}
MiniL.E.D Ramping mode	20s	2,2(0,1)^{a,b,c}	7,9(1,3)^{b}	49,7(8,8) ^{b,c,d}	39,0 (23,2)^{a,b}	8,0(1,3) ^{b,c}	6,2 (1,6)^{a,b,c,d}

Figure 9.1: Graphical representation of the contraction stress for all the 13 regimes. Homogenous subgroups are represented by linear markings.

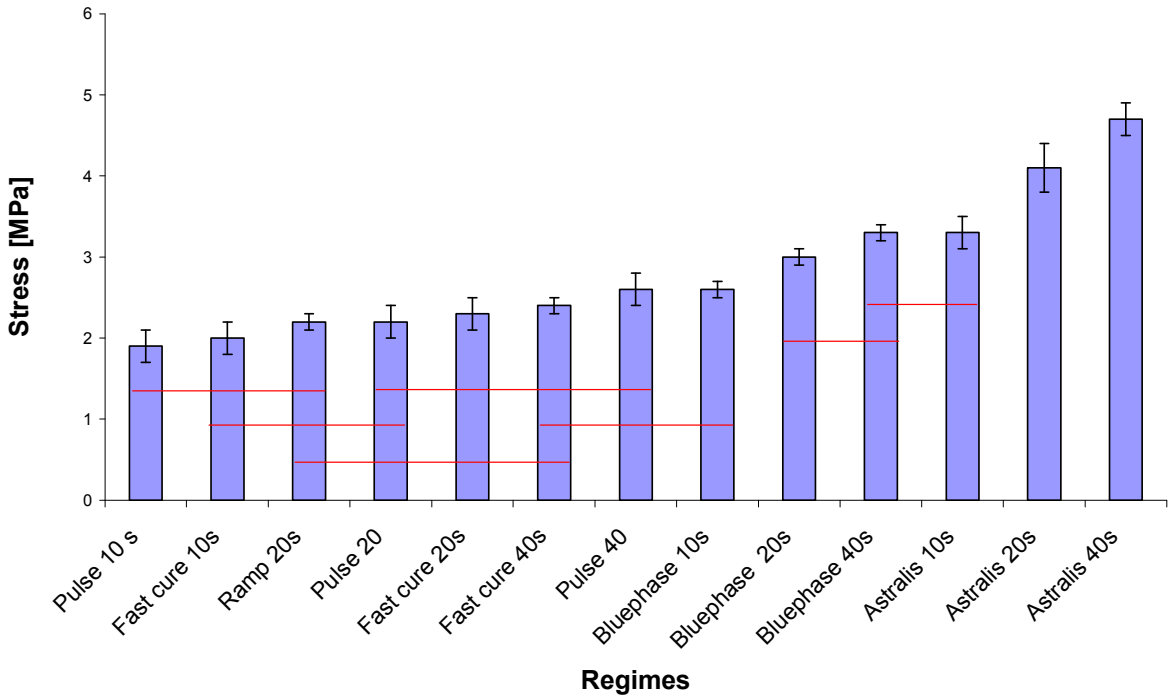


Figure 9.2: Comparison of the hardness values at the top and bottom surface of the polymerized composite for all the 13 regimes.

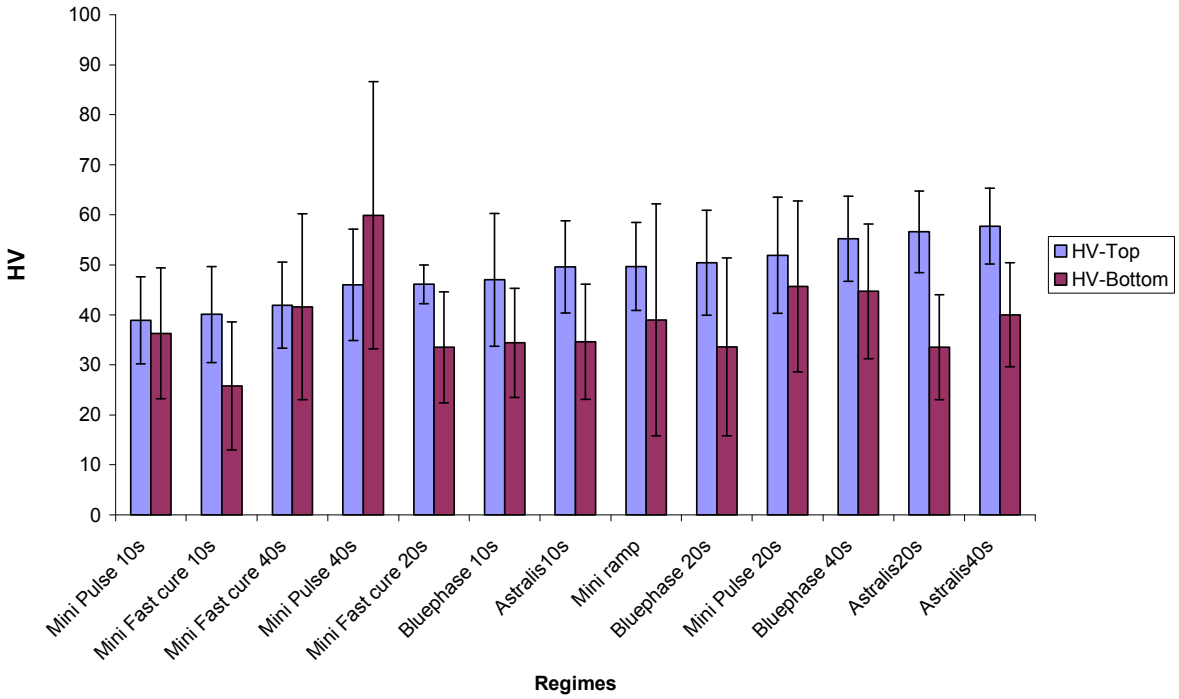


Figure 9.3: Modulus of elasticity values for all the 13 regimes. Homogenous subsets are represented by linear markings.

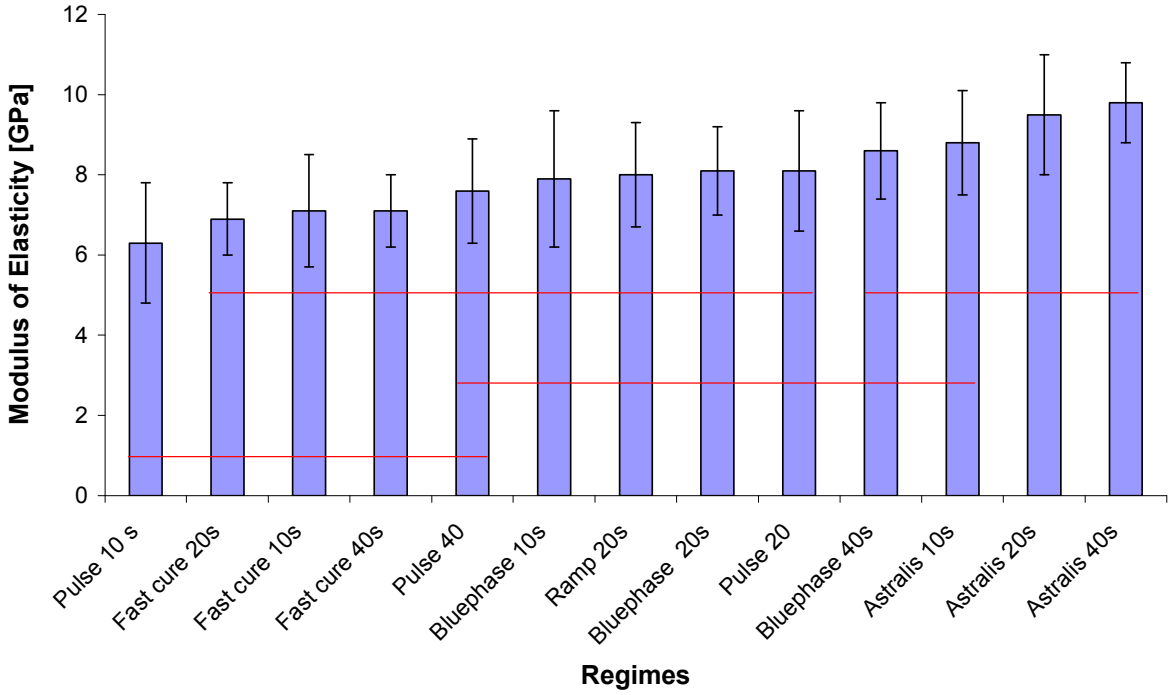


Figure 9.4: Gel points of Astralis 10, Bluephase, MiniL.E.D [Fast mode, Pulse mode and Ramping mode]. As seen with the other composites like Tetric Ceram, Tetric Evo Ceram and Filtek Supreme, the Ramping mode has the highest gel point for the composite Venus.

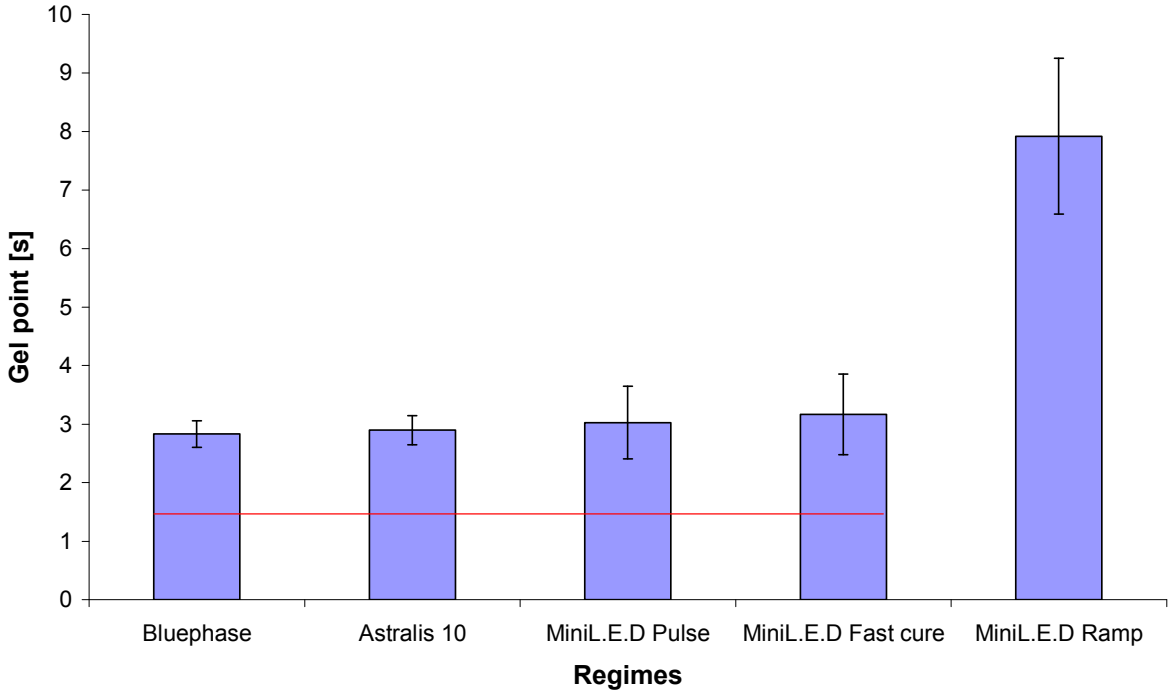


Figure 9.5: Shrinkage force curve forms for Astralis 10 for 10 s, 20 s and 40 s. There is a huge difference in the forms of the curves for the above mentioned exposure times indicating the change in the polymerization kinetics for different exposure times and the difference in the resulting contraction stress.

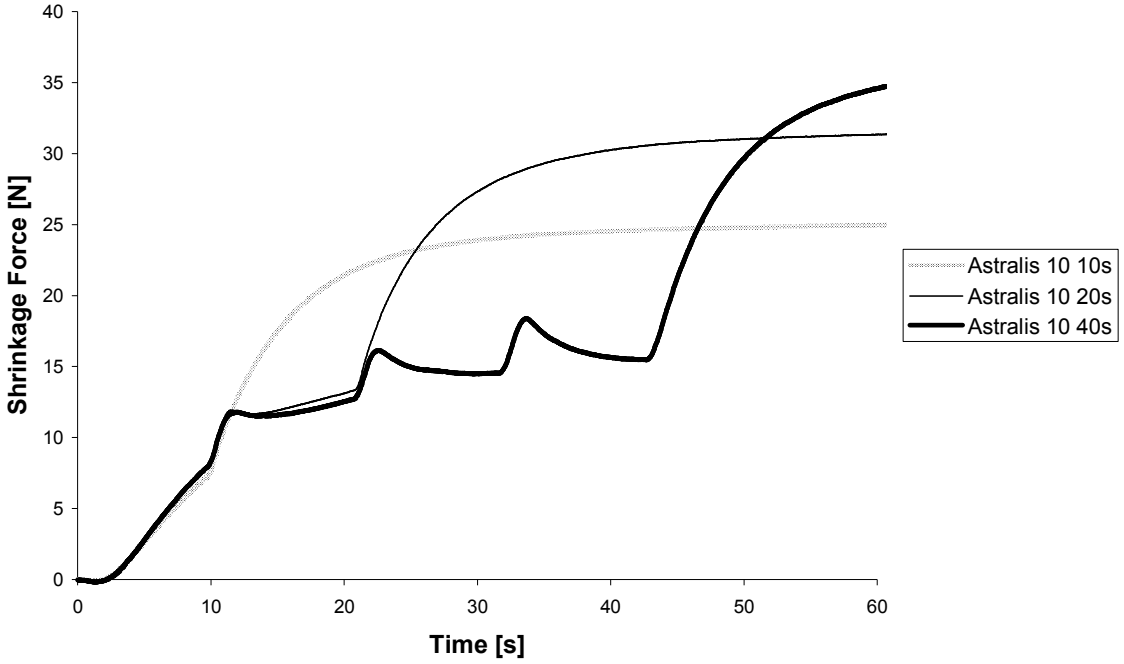
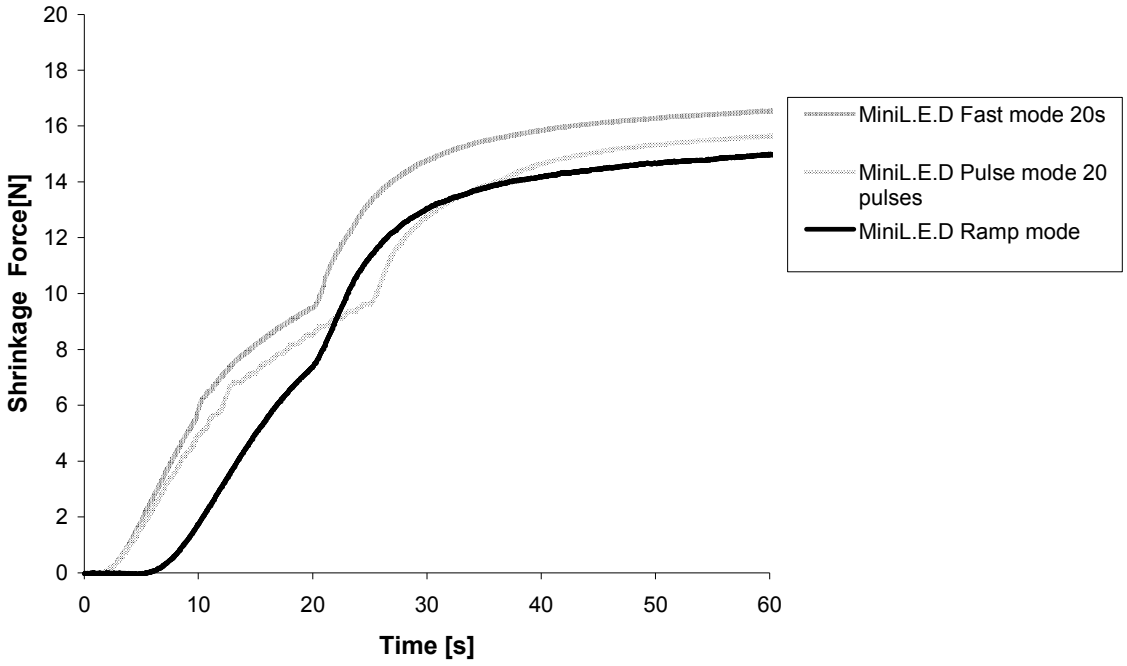


Figure 9.6: Comparison of the shrinkage curve forms for the LCU, MiniL.E.D for the 3 different modes namely Fast mode, Pulse mode and Ramping g mode for a period of 20 s. Though the inclination of the curves are comparable to each other, the time at which the curve turns up to form a steep inclination differs for ramping mode when compared to the other two modes indicating the slow gelation process.



Discussion: Mechanical properties can be improved with longer duration and higher light intensity. The mechanical properties correlate with the contraction stress (r = 0.75).The best mechanical properties were achieved with Astralis 10 (QTH) and Bluephase (L.E.D). The ramping and pulse modes of MiniL.E.D had the highest distance to the regression line indicating good mechanical properties and low shrinkage stress at the same

time. Thus it can be concluded that the modulation of light can effectively reduce curing stress and at the same time result in good mechanical properties.

Chapter 10

Comparison among Tetric Ceram, Tetric Evo Ceram, Venus and Filtek Supreme

In this chapter, a comparison of all the four composites namely Tetric Ceram, Tetric Evo Ceram, Venus and Filtek Supreme are made. The shrinkage curve patterns of all the four composites for an exposure time of 20s at 0mm are shown here.

Figure 10.1: Astralis 10 20s.

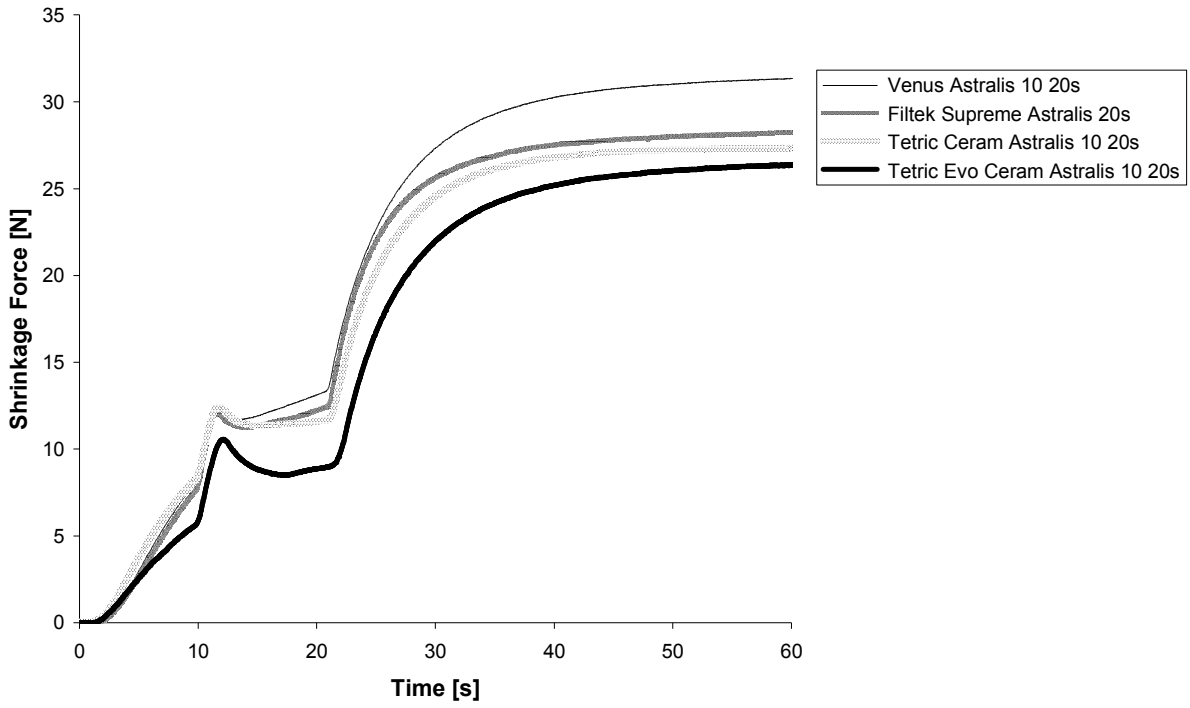


Figure 10.2: Bluephase 20s.

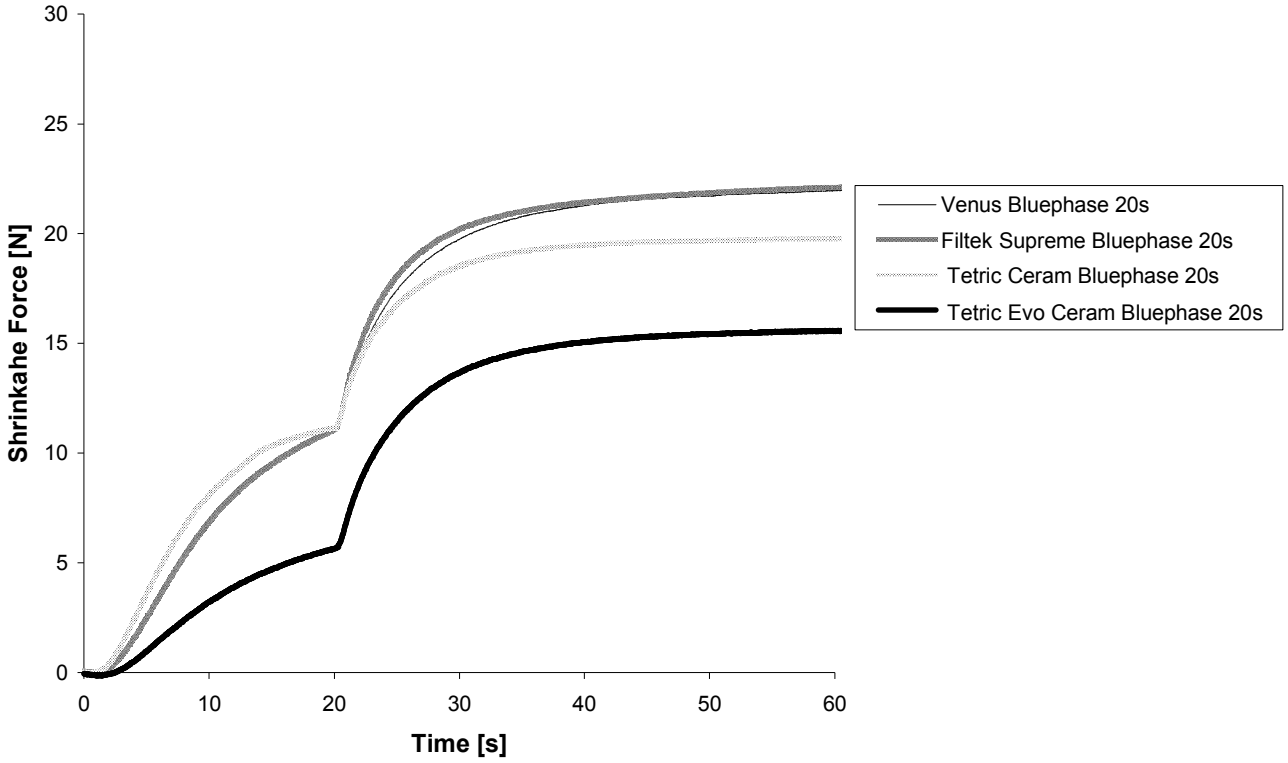


Figure 10.3: MiniL.E.D Fast mode 20 s

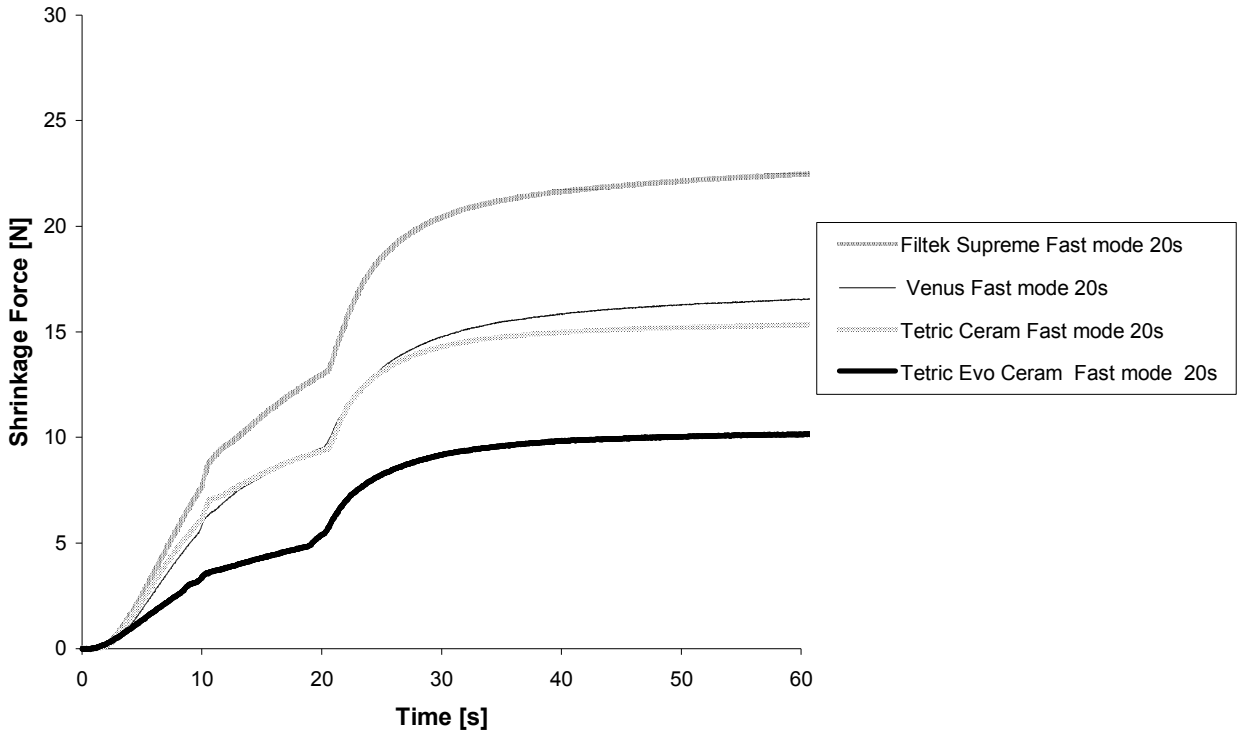


Figure10.4 : MiniL.E.D Pulse mode 20 pulses.

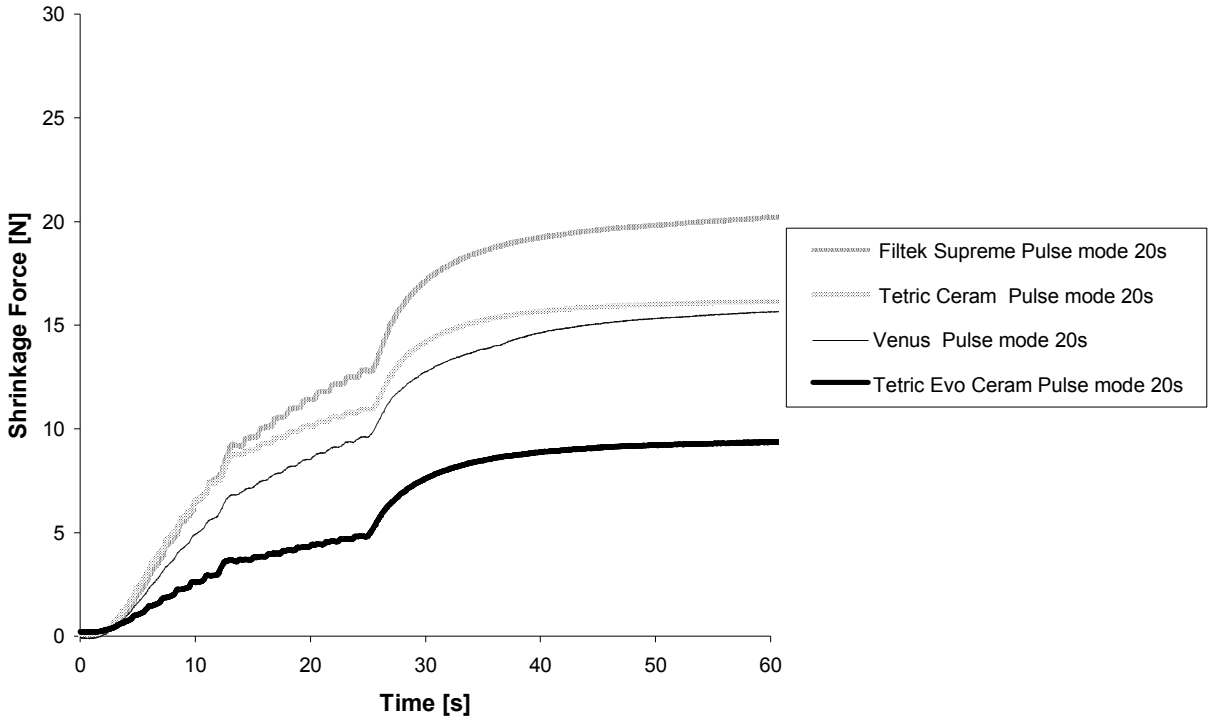
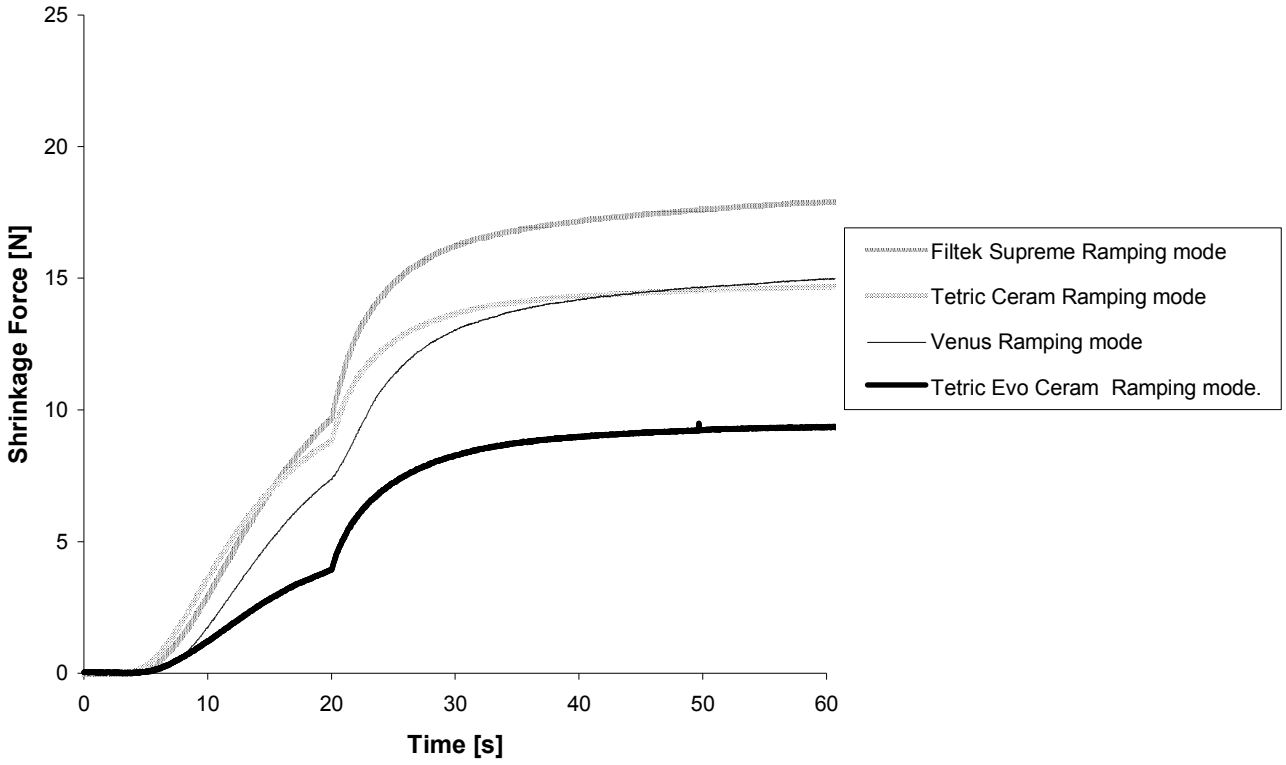


Figure 10.5: MiniL.E.D Ramping mode.



The shape of the curves by and large depends on the light intensity, exposure time, mode of curing and the type of the composite. Composite such as Tetric Evo Ceram with pre polymers have a low inclination of the curve than when compared to Filtek Supreme.

Figure 10.6: Comparison of the Hardness Value at the top surface for Tetric Ceram, Tetric Evo Ceram and Venus for all the 13 regimes. Since the Filtek Supreme study was not conducted for all the 13 regimes, the hardness values of that composite are not compared here.

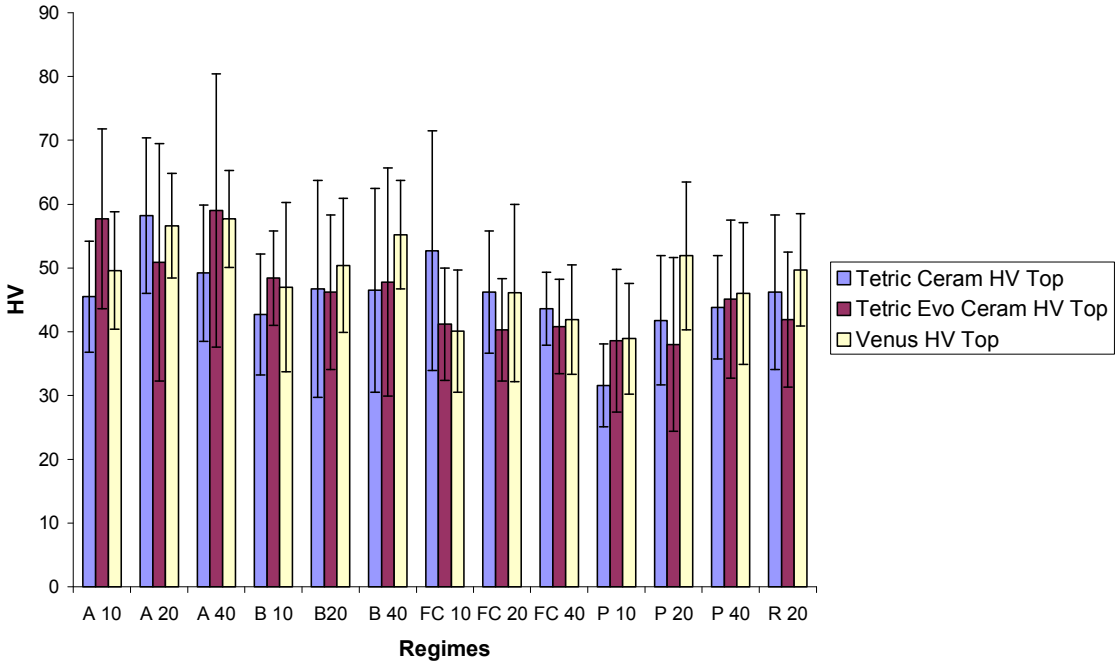
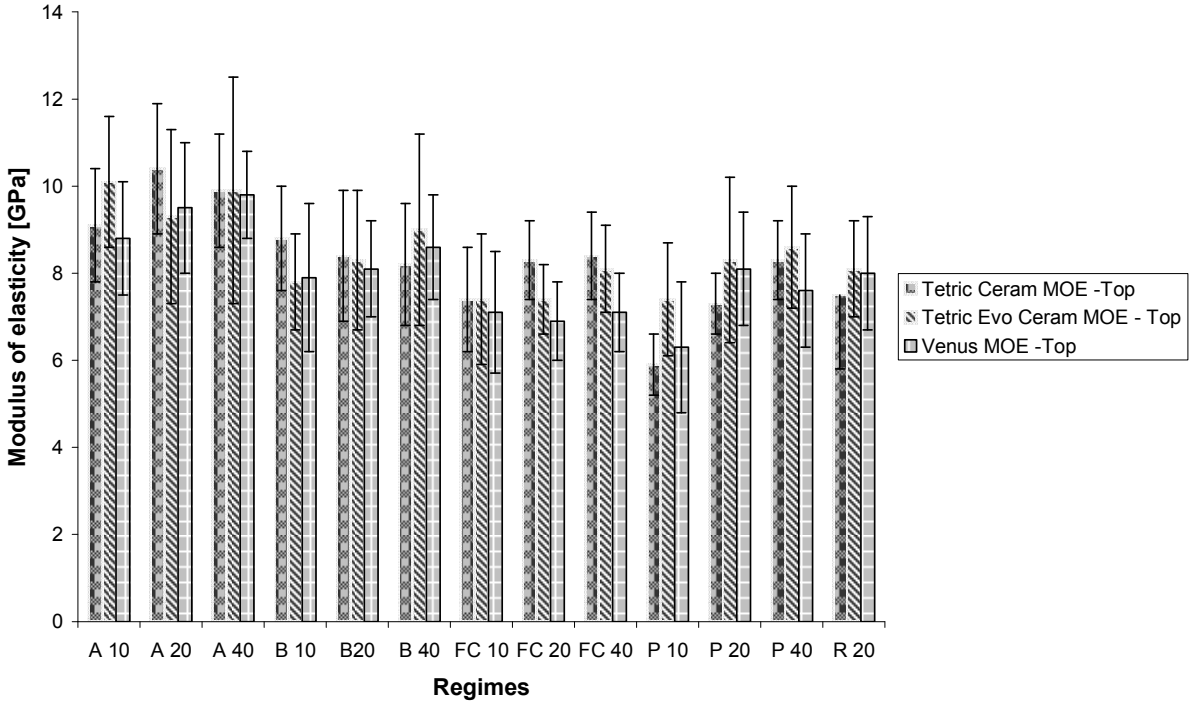


Figure 10.7: Comparison of the modulus of elasticity values for all the 13 regimes for the composites, Tetric Ceram, Tetric Evo Ceram and Venus. Filtek Supreme was not compared for the reasons as mentioned above.



Discussion:

The shrinkage curves for all the LCU for an exposure time of 20 s for all the four composites are shown. These curves are helpful to describe the curing behaviour of nanocomposites and micro hybrid which are the two main types that can be compared in this study. In all cases, Tetric Evo Ceram recorded the least contraction force. This advantage is due to fact that less amount of shrinkage is happening due to the presence of already shrunk prepolymers added to the inorganic component of the composite. The shrinkage curves are similar for Venus and Tetric Ceram. As both these composites are of the micro hybrid variety their shrinkage behaviour is similar for the L.E.D curing unit, MiniL.E.D. For the curing unit, Astralis

10, the difference in the behaviour is not very pronounced. Nanocomposite, Nanohybrid and Micro hybrid almost behave equally. This can be explained as a phenomenon of high intensity and temperature induced contraction.

In fact the shrinkage force of Venus *exceeds* that of Filtek Supreme when high intensity of Astralis 10 is applied. When Bluephase is used the shrinkage force of Venus is *equal* to that of Filtek Supreme. The shrinkage force is *low* for Venus than Filtek Supreme when MiniL.E.D is used. This is an apparent feature of Venus, which is more sensitive in the contraction behaviour as the light intensity is varied compared to the other 3 materials used in the study.

In a study conducted by Kleverlaan et al, the curing efficiency and heat generation of two high-intensity halogen lamps the Astralis 10 HIP (1100 mW cm(-2), and Optilux 501 Boost (1000 mW cm(-2) in curing three resin composites (InTen-S, Tetric Ceram, and Filtek Z250) were assessed. It was expected that the two lamps, having similar irradiance would give rise to the same curing efficiency and heat generation. The curing efficiency was evaluated by Vickers hardness and depth of cure measurements. No significant differences were observed in curing efficiency between the two lamps for the three resin composites. The temperature rise in the composites during curing was between 11.2 degrees C and 16.2 degrees C. At subsequent irradiation, after the composites had been cured, the temperature rise was between 8.2 degrees C and 12.1 degrees C. The Optilux 501 generated, in all cases, less heat than the Astralis 10. This was not expected based on the irradiance, but was accounted for by the differing spectra (Kleverlaan and de Gee, 2004).

With QTH lamps, the mean maximum resin composite sample thickness which cured sufficiently (relative surface ratio > or = 80%) was: 3 mm for Optilux 501, standard light guide, 40 s; 2.5 mm for Trilight, 40 s; and 1.5 mm for Astralis 10, 20 s (Ernst *et al,* 2004b).

Effectiveness of cure decreases with increased cavity depths. The mean hardness ratio at depths of 2mm, 3mm and more differ for halogen and LED curing units. Halogen lamps have greater ratios above 0.80 at 3mm whereas some LED does not achieve this ratio. For distances more than 3mm, the mean hardness ratio is ranked below the cut off value. Also the variations in the mode results in variations in the top and bottom hardness values. The depth of composite cure with LED LCUs was, therefore, product and mode dependent (Soh *et al,* 2003).

In a study conducted by Yap et al, Tetric Ceram was studied with Astralis 10 at 10 s and with conventional curing. This study investigated the effectiveness of cure and post-gel shrinkage. A strain-monitoring device was used to measure the linear polymerization shrinkage associated with the various composites and curing lights. The study concluded that polymerization was effective when Tetric Ceram was cured with conventional curing for 40 s than with Astralis 10 at 10 s. In view of the substantial time saving, using high intensity lights may be a viable method to polymerize composites (Yap *et al,* 2003).

Heat production is an important factor contributing to polymerization. At 3 mm, temperature rise observed with LED lights ranged from 4.1 degrees C to 12.9 degrees C, while halogen lights ranged from 17.4 degrees C to 46.4 degrees C. At 6 mm, temperature rise ranged from 2.4 degrees C to 7.5

degrees C and 12.7 degrees C to 25.5 degrees C for LED and halogen lights, respectively. Thermal emission of LED lights was significantly lower than halogen lights. Significant differences in temperature rise were observed between different curing modes for the same light and between different LED/halogen lights (Yap and Soh, 2003).

Though not of statistical significance, Venus is showing to do well than Tetric Ceram and Tetric Evo Ceram with regards to hardness values. On comparing the modulus of elasticity values, Tetric Evo Ceram is faring well.

Table 10.1: Hardness values at the top and bottom surface of all the four composites.

Light curing units	Tetric Ceram		Tetric Evo Ceram		Venus		Filtek Supreme	
	Top0	Bottom	Top0	Bottom	Top0	Bottom	Top0	Bottom
Astralis 10 (20 s)	58,2(12,2)	51,4 (16,3)	50,9 (18,6)	29,0 (16,9)	56,6(8,2)	33,5(10,5)	89,8 (10,7)	78,8(9,8)
Bluephase (20 s)	46,7 (17,0)	47,6 (15,5)	46,2 (12,1)	27,2 (13,6)	50,4(10,5)	33,6 (17,8)	74,2(6,0)	73,4(8,9)
MiniL.E.D Fast mode (20 s)	46,2 (9,6)	39,1 (11,9)	40,3(8,0)	28,3(20,0)	41,9(8,6)	41,6 (18,6)	59,0(5,0)	59,8(10,5)
MiniL.E.D Pulse mode (20 pulses)	41,8 (10,1)	40,3 (12,3)	38,0(13,6)	26,9(14,4)	46,0(11,1)	59,9 (26,7)	68,9(9,5)	66,8(14,7)
MiniL.E.D Ramping mode (20 s)	46,2 (12,1)	37,9 (12,9)	41,9(10,6)	30,1(14,5)	49,7(8,8)	39,0 (23,2)	60,5(4,8)	55,4(11,1)

The above tabulation of hardness values of all the four composites shows a stark contrast between the HV of Filtek Supreme and the rest of the composites. This huge difference in the property can be attributed to

1. The sample preparation: During the start of the study with Tetric Ceram and Tetric Evo Ceram, the samples were only abraded so as to remove the oxygen inhibited layer and minimal to no polishing was done on the samples. The samples were not regular and parallel to the measuring surface of the Fischerscope which could have affected the readings. These short comings were minimized during the sample

preparation of Filtek Supreme. Polishing was given importance and more samples were repeated. Also, an extra measure was taken to prepare plane samples in special disks which helped to minimise the standard deviation. A change in the sample preparation methodology proved to be effectively improving the hardness values. This explains the reason why all composite restorations must be carefully finished and polished so as to improve the strength and hardness of the restoration.

2. Nanocomposites: The hardness value of Filtek Supreme by virtue of its chemical composition tends to achieve more hardness than micro hybrids.

Table10.2 : Modulus of elasticity achieved at the top surface for all the four composites.

Regimes	Tetric Evo Ceram	Tetric Ceram	Venus	Filtek Supreme
Astralis 10 20s	9,7 (2,0)	10,4 (1,5)	9,5 (1,5)	12,7 (2,0)
Bluephase 20s	8,3(1,6)	8,4(1,5)	8,1 (1,1)	11,0 (1,1)
Fast mode 20s	7,4 (0,8)	8,3 (0,9)	6,9 (0,9)	9,5 (0,8)
Pulse mode 20 pulses	8,5 (1,8)	7,3 (0,6)	8,1 (1,5)	10,8 (0,9)
Ramping mode- 20s	8,2 (1,1)	7,5 (1,7)	8,0 (1,3)	10,3 (0,7)

The modulus of elasticity is high for Filtek Supreme and low for Venus.

Chapter 11

Summary

Evaluation of dental composite by its materialistic properties is the path leading to improvements in long term restorations. Various shades and flow of composites mainly bring about natural replication of teeth provided proper restorative techniques are followed. While the key point in patient satisfaction being good aesthetics of composites, this can not be achieved without good care for material properties. The end result is interdependent on factors which influence the longevity and stability of the restoration in the oral cavity along with biocompatibility factors. If a composite has poor wear resistance and hardness, then the period for which the restoration is present in the mouth is fairly reduced. Highly contracting composite will cause micro cracks in the enamel due to stress, which traps debris and impairs the aesthetics. For a composite restoration to be aesthetically successful other properties such as polymerization shrinkage and mechanical properties should be favourable. With this in mind, the main factors which had been influencing the material properties of composites are studied.
In this study, the discussion will be based on the comparison of Tetric Ceram (micro hybrid), Tetric Evo Ceram (nanohybrid, Ceromer), Venus (micro hybrid) and Filtek Supreme (Nanocomposite). It is a basic study to see if there existed any difference between high and low intensity lamps, and between halogen and LED lamps. Each of the composites reacted in a different way to the light and heat from the LCU.

1. Shrinkage characteristics: Let us first consider the shrinkage curves of all the composites. All of them have a phase of relaxation but this phase is by

and large dependent on the distance of the LCU and the heat from the source. The aim is always to increase this phase of relaxation. This is because of the fact that this relaxation will provide more time for the bond strength to be gained. Of the four composites Venus flows for a longer time for Astralis10; Tetric Evo Ceram for the LC regimes of Bluephase and MiniL.E.D Fast and Pulse mode and again Venus for the Ramping mode. Tetric Ceram cures fast for all regimes and for all curing units. Though Tetric Ceram has fast polymerization rate, the stress is not the highest. The nano composite Filtek Supreme and Venus recorded high stresses among the four composites. This indicates that gel point alone is not a factor to reduce stress. For all curing units (except Astralis 10), Tetric Evo Ceram has high gel point and low stress. Based on stress production, Tetric Evo Ceram will be voted the best among the four composites.

2. Hardness: Though, reducing stress is an important criterion in determining the restoration's quality, the hardness values is as important as the stress values. A high hardness value represents high degree of conversion and wear resistance. In this study, all the hardness measurements were done immediately. The main aim was not to measure the hardness values but only to know if adequate curing has occurred or not. For the Filtek Supreme study alone the hardness was studied exclusively to determine both 0 h and 24 h hardness values. Separate samples were prepared in special plastic discs. Hardness was measured after sand papering with 1200 grit silica followed by polishing with a suspension of diamond (1 to 3 μm) in alcohol. It is feared that this alcohol in the polishing agent could have influenced the post curing of the composite after storage in water. For comparison purposes the hardness values for Filtek Supreme is not used. The study for distances with Tetric Ceram was conducted without polishing as during this study, the

aluminium attachments were not separated from the sample after force measurements. Thus only abrading of the oxygen–inhibited layer was done. The procedures for Venus and Tetric Evo Ceram and Tetric Ceram with different regimes were similar in that the samples were separated from the aluminium attachments with minimal force so that no additional internal stress was intended to be incorporated which could alter the hardness values. Both grinding and polishing procedures were followed. The samples from the shrinkage machine were not perfectly planar samples and this was one reason why it was hard to measure the samples without high standard deviations. In order to avoid this problem, the Filtek Supreme HV was done separately. When the HV for Tetric Ceram, Tetric Evo Ceram and Venus are compared, no significant differences are noted and for all the above said composites, Astralis 10 yielded the highest hardness values. The HV attained by Filtek Supreme was twice as much as the other composites, the reason behind being the sample preparation methodology. High degree of polishing is surely enhancing the HV. This is one good reason why polishing should be considered not just as the last finishing step but a prime procedure to be done with utmost care. The equal degree of hardness among the three composites may be attributed to the equality in filler volume and the residual monomer (Martos *et al*, 2003).

3. Modulus of elasticity: Micro-indentation tests are a reliable test method for the determination of elastic properties of composite (Chung *et al,* 2005). The polymerisation shrinkage stress builds up in a time when there is high conversion during the latter stages of polymerization. During this vitrification stage the elastic modulus increases dramatically. Increase in the elastic modulus and cooling of the sample after an exothermic reaction of

polymerisation contributes to the overall stress (Lu *et al,* 2004b). When non-flowable materials are over a flowable material, the elastic modulus of the liner, in this case, flowable composite determines the stress reduction. On the other hand, flowable composite acting as restoratives does not lead to reduced stress production. They are not statistically significantly different from the non-flowables (Braga *et al,* 2003). In fact flowables have higher shrinkage than the non-flowables (Labella *et al,* 1999). This leads to higher interfacial stresses. Composites with coarse macro filler have modulus of elasticity that is higher than those of fine macro-fillers (Bryant and Mahler, 1986).

In the Filtek Supreme study, the modulus of elasticity increased after 24 h for all distances. This clearly demonstrates that water sorption at 24 h did not soften the matrix system of the material. This is strengthened by the fact that the creep values at 24 h were less than that at 0 h. The CIT_1 and CIT_2 values at 0 h were in the range of 3.7 to 4.7 and -4.5 to -5.3 respectively in comparison to 3.4 to 3.4 for CIT_1 and -3.7 to -4.2 for CIT_2 at 24 h. Water sorption increases the creep values and decreases the modulus of elasticity values Also the creep values decrease and the modulus of elasticity values increase with the amount of filler content (Oysaed and Ruyter, 1986).

Chapter 12
Conclusion

When the four composites namely Tetric Ceram, Tetric Evo Ceram, Filtek Supreme and Venus are studied for their polymerisaton shrinkage stress and mechanical properties, it is concluded in this study that each composite has advantages and disadvantages. Tetric Ceram and Venus have intermediate properties in that they have acceptable level of mechanical properties and not very high polymerisation stress levels. Tetric Evo Ceram shows low polymerisation stress values for all the light curing units used in the study but has a potential problem of attaining only lower hardness values. Since this hardness value before post curing alone can not be taken as a guide to comment on the material as a whole, more studies into Tetric Evo Ceram pertaining to its mechanical properties should be done. Filtek Supreme has very good mechanical properties as well as high polymerisation stress values which again is one of its limitations. From this study, I conclude that more experiments have to be done until we have maximum allowable polymerisation shrinkage and stress range for the different types of dental composite which could be safely used on the patient so as to maintain the standard of composite restorations. Some composite qualities such as degree of conversion, fracture toughness, strength, and biocompatibility are beyond the scope of this study. Also, the relevance of these laboratory based experiments to the clinical situation should be analysed.

In order to come to a conclusion as to which light curing unit has done the best two criteria are set .They are low polymerisation shrinkage stress and

high hardness value. It is more likely that Astralis 10 always produced high polymerisation shrinkage for all the 4 composites which is not desirable. The hardness values yielded were not superior to that produced by Bluephase and MiniLED. Therefore the use of this halogen light curing unit can not be supported because it produced very high stress but did not cure the material properly at 10 s which it is supposed to achieve. Bluephase produced intermediate properties whereas out of the three light curing units, MiniLED produced the lowest polymerisation shrinkage stress and yielded good hardness value which matches the criteria that was formulated. Out of the three different modes in MiniLED, Ramping mode produced the least stress for all the composites. So of the three light curing units, MiniLED excels Astralis10 and Bluephase in terms of producing low polymerisation stress and also acceptable hardness value taking into consideration the limitations of the study. FTIR analyses will shed more light to find the differences between the different modes in MiniLED.

The interaction of the light curing units and the different types of dental composites is evident from this study. For example, Filtek Supreme was able to produce low stress when cured with MiniLED whereas the same material produced relatively high stresses when polymerised by Astralis 10. So, composite dentistry will have to take into consideration that material properties are modifiable in a dentist’s office. Each composite will be influenced by the type of light curing unit, time given for curing , distance at which it is cured and intensity of light.

Chapter 13
Zusammenfassung

Der Vergleich der vier kommerziellen Komposite Tetric Ceram, Tetric Evo Ceram, Filtek Supreme und Venus zeigte, dass sie hinsichtlich ihrer mechanischen Eigenschaften und Polymerisationsschrumpfung sowohl Vor- als auch Nachteile in sich vereinen.

Tetric Ceram und Venus haben durchschnittliche mechanische Eigenschaften, dafür hält sich die Spannung in Folge der Polymerisationsschrumpfung in akzeptablen Grenzen. Tetric Evo Ceram weist im Zusammenhang mit allen Polymerisationslampen niedrige Kontraktionsspannungen auf, was im Zusammenhang mit der Randspaltneigung positiv ist, erzielt jedoch nur geringe Härtewert. Filtek Supreme hat gemessen an der Universalhärte sehr gute mechanische Eigenschaften, gleichzeitig treten jedoch auch hohe Polymerisationsspannungen auf, was in bestimmten Situationen eine Limitation darstellen kann.

In dieser Dissertation wurde überwiegend die Polymerisationsschrumpfung und stellvertretend für die mechanischen Eigenschaften die Universalhärte sowie der E-Modul auf Druck untersucht. In weiteren Studien sollten auf jeden Fall auch die Umsatzraten, Biegefestigkeit und –zähigkeit untersucht werden, um den optimalen Kompromiss zwischen guten mechanischen Eigenschaften und geringer Polymerisationsschrumpfung definieren zu können.

Im Zusammenhang mit dem Polymerisationsregime kann man festhalten, dass Polymerisationslampen vom Typ Astralis 10 mit hoher Lichtintensität vermutlich aufgrund der hohen Umsatzrate bei der Polymerisation immer auch hohe Kontraktionsspannungen zufolge haben. Dies galt für alle vier untersuchten Kompositwerkstoffe. Die Universalhärte, die mit Astralis 10 erreicht wurde, unterschied sich nicht wesentlich von der Härte, die mit den Lampen Bluephase und MiniLED erzielt werden konnten. Trotz aller Vorteile des breitbandigen Halogenlichtspektrums scheint die Anwendung der Polymerisationslampe Astralis 10 bei hoher Lichtintensität und kurzer Belichtungsdauer nicht wünschenswert zu sein. Innerhalb der Gruppe der drei Polymerisationslampen erzielte die Lampe Bluephase überdurchschnittliche Ergebnisse. Die Lampe im MiniLED hatte die geringsten Polymerisationsspannungen zur Folge und erzielte gleichzeitig eine gute Universalhärte, so dass ihr Einsatz im Rahmen der vorliegenden Befunde befürwortet werden kann.

Die Polymerisationslampe MiniLED meist drei verschiedene Belichtungsmodi auf, wobei der so genannte “ramp cure mode” die besten Ergebnisse erzielte. Es muss jedoch eingeschränkt werden, dass erst eine gezielte FTIR Analyse Unterschiede hinsichtlich der Umsatzraten überprüfen muss.

Die Studie zeigte deutlich, dass eine intensive Interaktion zwischen Polymerisationslampe und Füllungswerkstoff zu beobachten ist. Filtek Supreme erzielte beispielsweise im Zusammenhang mit der Polymerisationslampe MiniLED niedrige Kontraktionsspannungen,

während die Kontraktionsspannungen bei Anwendung der Lampe Astralis 10 sehr hoch waren. Aus diesem Grund ist es derzeit nicht trivial, die optimale Kombination hinsichtlich Belichtungsintensität, Belichtungsdauer, Intensitätsmodulation und sogar Abstand zwischen Polymerisationslampe und Werkstoff zu formulieren. Weitere systematische Untersuchungen können jedoch dazu beitragen, diese Zusammenhänge weiter zu verfeinern.

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ANURADHA VISVANATHAN B.D.S,
3, Marley Croft, Moor Lane, Staines
TW18 4YW
Tel: 00441784454561
visvanathananuradha@yahoo.com, anuvish2@rediffmail.com

OBJECTIVE:

As an upcoming dentist, I am aiming to pursue my career in clinical dentistry and dental research.

ACADEMIC BACKROUND:

Dental Research (July 2004-Nov 2005) : Dissertation (Doktorarbeit) at Ludwig Maximilians University, Munich, Germany.
Research Topic: Influence of various light curing units on the polymerization shrinkage stress and mechanical properties of composites.
Presentations and Conferences: Research papers were presented at the

1. 83rd General Session of the International Association for Dental Research (IADR), Baltimore, March 2005
2. Continental European Division (CED) and Scandinavian Division (NOF) of IADR, Amsterdam, September 2005
3. 35th Annual meeting of American Association of Dental Research, AADR, Orlando, March, 2006

Publications:
1.Visvanathan A, Ilie N, Hickel R, Kunzelmann KH:The influence of curing times and light curing methods on the polymerization shrinkage stress of a shrinkage-optimized composite with hybrid-type prepolymer fillers.Dent Mater. 2007 Jul; 23(7): 777-84
2. Ilie N, Kunzelmann KH, Visvanathan A, Hickel R:Curing behavior of a nanocomposite as a function of polymerization procedure.Dent Mater J. 2005 Dec; 24(4):469-77.
Research Experience:

- Determination of polymerization shrinkage stress of light cure composites using Stress-Strain analayser.
- Determination of mechanical properties like hardness value, modulus of elasticity and creep of composites using Fischerscope.

- Statistical analyses of data using SPSS software.
- Team work for projects for the determination of shrinkage stress and degree of conversion for newly developed composites with various researchers including those from foreign universities.
- Involved in preparing manuscripts of research work for dental journals.

PROFESSIONAL QUALIFICATION:

BACHELOR OF DENTAL SURGERY-(B.D.S)

Year of Passing : November 2001

Internship (C.R.R.I) Completion : December 2002

University **:** The Tamilnadu Dr. M.G.R Medical University, Chennai, India

College **:** Sree Balaji Dental College and Hospital, Chennai, India

Registration Number : 6486

WORK EXPERIENCE:

- Anterior & posterior root canal treatments.
- Tooth Preparation for Crown.
- Extractions, assisting impactions, and periapical surgeries.
- Handling composites for anterior & posterior restorations &also various other dental cements.
- Splinting of teeth.
- Attended Surgical Procedures as a non-participant observer (Orthognathic Surgeries, Mandiblectomy, Neurectomy, and Intermaxillary Fixation in cases of Fracture of Maxilla & Mandible) in Hospitals.
- Gingivectomy & Flap Surgeries.
- Attended various dental camps, dental health education programmes and patient motivation programmes.
- Continuing education in the fields of dentistry.
- Attended Seminars, Hands-On Courses and Conferences.

AREAS OF INTEREST: Material sciences, Oral pathology & Endodontics.

SCHOOLING:

HIGHER SECONDARY EDUCATION-(XI & XII std.) 1995 to 1997
Studied at "Shrine Vailankanni Matriculation Higher Secondary School", Chennai.
Score**:** Higher Secondary Examination, 90 %

SECONDARY SCHOOL EDUCATION-(X std)-1994 to 1995
Passed with Distinction the "All India Secondary School Examination" (AISSE) of the "Central Board Of Secondary Education" (CBSE) held in March 1995**,** from "Shrine Vailankanni Senior Secondary School", Chennai.

JUNIOR GRADES (1984 TO 1995)
Studied at the "Shrine Vailankanni Senior Secondary School", Chennai, Tamilnadu, India
Medium of Instruction at School & College: **ENGLISH**
Languages Known : English, Tamil, Hindi and German

PERSONAL BACKROUND:
Date of Birth : 21st November 1979.
Place of Birth : Tiruchirapalli, Tamilnadu, India
Nationality : INDIAN
Marital Status : Married